1961

Cadmium Halide Complexes and Anion Exchange Equilibria.

Edward Lyndol Harris
Louisiana State University and Agricultural & Mechanical College

CADMIUM HALIDE COMPLEXES AND ANION EXCHANGE EQUILIBRIA

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Department of Chemistry

by
Edward Lyndol Harris
B. A., McMurry College, 1956
M. S., Louisiana State University, 1958
June, 1961

ACKNOWLEDGMENT

The author wishes to gratefully acknowledge the advice and assistance given to him on numerous occasions by Professor Maurice M. Vick, who directed this work.

TABLE OF CONTENTS

	Page
INTRODUCTION	1
EXPERIMENTAL PROCEDURES	8
Reagents and Analytical Methods	8
Equilibrium Determinations	9
Resin Volume Determinations	11
RESULTS	14
Resin Volumes	14
Equilibrium Distributions	17
TREATMENT OF DATA	25
Cadmium Halide Complexes	25
Program for the IBM 650 Computer	31
The Calculation of Activity Coefficient Ratios and Resin Phase Activity Coefficients	38
DISCUSSION	71
CONCLUSION	85
SELECTED BIBLIOGRAPHY	87
VITA	93

LIST OF TABLES

Table		Page
I.	Resin Volumes	15
II.	Equilibrium Concentrations in the Cadmium Chloride-Resin Chloride System	19
III.	Equilibrium Concentrations in the Cadmium Bromide-Resin Bromide System	20
IV.	Equilibrium Concentrations in the Cadmium Iodide-Resin Iodide System	21
V.	Equilibrium Concentrations in the Cadmium Nitrate-Resin Chloride System	22
VI.	Equilibrium Concentrations in the Cadmium Nitrate-Resin Bromide System	23
VII.	Equilibrium Concentrations in the Cadmium Nitrate-Resin Iodide System	24
VIII.	Calculated Ionic Concentrations for the Cadmium Chloride-Resin Chloride System	39
IX.	Calculated Ionic Concentrations for the Cadmium Bromide-Resin Bromide System	41
X.	Calculated Ionic Concentrations for the Cadmium Iodide-Resin Iodide System	43
XI.	Calculated Ionic Concentrations for the Cadmium Nitrate-Resin Chloride System	45
XII.	Calculated Ionic Concentrations for the Cadmium Nitrate-Resin Bromide System	47

Table		Page
XIII.	Calculated Ionic Concentrations for the Cadmium Nitrate-Resin Iodide System	49
XIV.	Calculated Ionic Concentrations for the Cadmium Chloride-Resin Chloride System	51
XV.	Calculated Ionic Concentrations for the Cadmium Bromide-Resin Bromide System	53
XVI.	Calculated Ionic Concentrations for the Cadmium Iodide-Resin Iodide System	55
XVII.	Calculated Ionic Concentrations for the Cadmium Nitrate-Resin Chloride System	57
XVIII.	Calculated Ionic Concentrations for the Cadmium Nitrate-Resin Bromide System	59
XIX.	Calculated Ionic Concentrations for the Cadmium Nitrate-Resin Iodide System	61
XX.	Activity Coefficient Ratios and Resin Phase Activity Coefficients for Cadmium Chloride in the Cadmium Chloride-Resin Chloride System	65
XXI.	Activity Coefficient Ratios and Resin Phase Activity Coefficients for Cadmium Bromide in the Cadmium Bromide-Resin Bromide System	66
XXII.	Activity Coefficient Ratios and Resin Phase Activity Coefficients for Cadmium Iodide in the Cadmium Iodide-Resin Iodide System	67
XXIII.	Activity Coefficient Ratios for Cadmium Chloride in the Cadmium Nitrate-Resin Chloride System.	68
XXIV.	Activity Coefficient Ratios for Cadmium Bromide in the Cadmium Nitrate-Resin Bromide System.	69
XXV.	Activity Coefficient Ratios for Cadmium Iodide in the Cadmium Nitrate-Resin Iodide System.	70
XXVI.	Activity Coefficient Ratios and Resin Phase Activity Coefficients for Cobalt Chloride and Barium Chloride.	72

LIST OF FIGURES

Figure		Page
1.	Centrifuge Apparatus for Resin Wet Weight Determinations	13
2.	The For Transit Program	33
3.	Sample of a For Transit Data Form	36
4.	Stoichiometric Activity Coefficient Ratios of the Cadmium Halides *vs.* Cadmium Halide Molarity in the External Solution	75
5.	Stoichiometric Activity Coefficients of the Cadmium Halides in the Resin Phase *vs.* Cadmium Halide Molarity in the External Solution	76
6.	The Calculated Actual Mean Ionic Activity Coefficients of Cadmium Chloride in the Resin Phase *vs.* Cadmium Chloride Molarity in the External Solution . .	77
7.	The Calculated Actual Mean Ionic Activity Coefficient of Cadmium Bromide in the Resin Phase *vs.* Cadmium Bromide Molarity in the External Solution . .	78
8.	The Calculated Actual Mean Ionic Activity Coefficients of Cadmium Iodide in the Resin Phase *vs.* Cadmium Iodide Molarity in the External Solution	79

ABSTRACT

The equilibrium distribution of a diffusible electrolyte between an aqueous solution and an ion exchange resin can be expressed as a ratio of mean ionic molar concentrations in each of the two phases. If the same standard state is chosen for both phases, then the reciprocal of the ratio of the mean ionic concentrations is equal to the corresponding ratio of mean ionic activity coefficients. The activity coefficient ratios can be combined with activity coefficients for an electrolyte in aqueous solutions to give activity coefficients for the electrolyte in the resin phase.

Stoichiometric mean ionic activity coefficients were obtained in this way for cadmium chloride, cadmium bromide and cadmium iodide in the respective chloride, bromide and iodide forms of a strong-base anion exchange resin (Dowex-1). Since complexation reactions presumably occur in these systems, an attempt was made to separate this complexation effect from the stoichiometric activity coefficients.

Actual mean ionic activity coefficient ratios were calculated from estimates of the concentrations of free (hydrated) cadmium ion and halide ion present in each of the two phases. These concentrations were obtained by use of the complex formation constants available in the literature. In order to calculate resin phase activity from these ratios, the necessary actual mean ionic activity coefficients for the cadmium salts in the external solutions were taken to be the geometric

means of the individual ion activity coefficients from Kielland's table.

The stoichiometric mean activity coefficients for the cadmium halides in the resin phase were found to be twenty to forty times smaller than those given in the literature for barium and cobalt chlorides at similar external solution concentrations. Conversely, values of the actual mean ionic activity coefficients for cadmium chloride and cadmium bromide were about three times larger than the stoichiometric activity coefficients for barium chloride and cobalt chloride. Thus it appears that the very low values for the stoichiometric activity coefficients of cadmium chloride and cadmium bromide in the resin may be attributed almost entirely to extensive formation of cadmium halide complex ions in that phase.

The actual mean ionic activity coefficients for cadmium iodide in the resin were found to be unreasonably large. However, these values were calculated with the assumption of a maximum coordination number of four for the cadmium halide complex ions. Resin loading data suggest that this assumption is not legitimate in the case of cadmium iodide. Instead, a maximum coordination number of five or six appears to be more probable for this system.

INTRODUCTION

In recent years the use of synthetic ion exchange resins has attained a prominent position in the growing list of methods and techniques available to the analytical chemist. Thousands of publications have appeared in the literature concerning chemical separations effected by use of various types of both cation and anion exchangers. Reviews are published frequently on these and other analytical aspects (12).

Ion exchange resins have been found to be useful to the analyst in implementing other techniques, such as in the concentrating of dilute solutions prior to analysis (6), and in increasing the sensitivity of spot tests (27). Such practical applications will no doubt continue to flourish in years to come, especially as the properties of the resins become better understood and as the techniques for producing the resins are expanded and improved.

Apart from the investigations concerned mainly with developments of a practical nature, there has been considerable basic research into the physical chemistry of ion exchange resins. A recent and comprehensive review along these lines has been made by Kitchener (5). Reviews also appear regularly in the Annual Review of Physical Chemistry (13). Ion exchange resins offer a novel approach to the study of electrolytes in concentrated solutions that perhaps will prove to be of value in this area of physical chemistry which is

presently beset with many difficulties.

The equilibria established between ion exchange resins and external solutions of electrolytes may be classified in one of two general types: a) non-exchange equilibria between a resin and a diffusible electrolyte with an ion common to both, and b) exchange equilibria between a resin and a diffusible electrolyte without an ion common to both. The former type does not involve ion exchange in the usual sense of the term and is somewhat less difficult to treat theoretically. The method of treatment is formally the same for both cation and anion exchange resins, but only the strong-base anion exchangers will be considered here.

Kraus and Moore (25), Gottlieb and Gregor (18), and Nelson and Kraus (28) have investigated the non-exchange type of equilibria for strong-base type anion exchange resins in equilibrium with aqueous solutions of various electrolytes over wide ranges of electrolyte concentration. The general procedures employed by these workers were the same. The experimentally determined quantities were the molalities of the diffusible ions in both phases. The ratios of the mean ionic activity coefficients in the two phases were then calculated by use of the relation

$$\frac{\bar{f}_{\pm}}{f_{\pm}} = \left(\frac{m_1^{\nu_1} m_2^{\nu_2}}{\bar{m}_1^{\nu_1} \bar{m}_2^{\nu_2}} \right)^{1/\nu}$$

where m_1 and m_2 are the molalities of cation and anion, respectively, and $\nu = \nu_1 + \nu_2$ in the usual notation. A bar over a quantity indicates that the quantity pertains to the resin phase.

The above relation implies that the same standard state is used for the diffusible electrolyte in both phases. It was thus derived directly by Kraus and Moore (25) without assuming a particular model for the resin phase, but was derived by Gregor (19) from Gibbs-Donnan considerations with neglect of the pressure-volume term in the final result. The activity coefficient ratios obtained in this way may then be combined with the known activity coefficients of the electrolytes in ordinary aqueous solutions to give mean activity coefficients for the diffusible electrolyte in the resin phase.

It is not possible at present to give an interpretation of activity coefficients for electrolytes in other than very dilute solutions. However, activity coefficients for different electrolytes in the same type of ion exchange resin may be compared with each other, or they may be compared with activity coefficients obtained in ordinary aqueous solutions of mixed electrolytes at high concentrations. This latter approach is often hindered by the lack of suitable data for aqueous solutions (28).

The activity coefficient data presented by the authors mentioned in the preceding paragraphs were for electrolytes which

apparently do not form complex ions, although they may be associated in other ways (e.g., alkali halides, alkaline-earth halides, etc.). Activity coefficients obtained in the present work are for the chloride, bromide and iodide salts of cadmium. These compounds are believed to exist in solution chiefly in the form of complex ions down to salt concentrations as low as 0.01 moles per liter or less.

In studying the anion exchange behavior of systems where anionic metal complexes are involved, the experimental procedure has almost invariably been one of measuring the equilibrium distribution of small amounts of central metal ion as a function of ligand concentration in the external solution. The results have been most frequently reported in the form of distribution curves, wherein a distribution coefficient (defined as D = concentration of central metal in resin / concentration of central metal in external solution) is plotted vs. ligand concentration in the external solution. Kraus and co-workers (7) at Oak Ridge have determined the distribution curves for various oxidation states of practically every metal in the periodic table, using hydrochloric acid as the ligand source in the external solution. A maximum in the distribution curve was found for many of the metal ions. However, a maximum was never reached for some metals, and for a few the maximum occurred at so low a ligand concentration as to be scarcely detectable if it occurred at all.

In 1953 Fronaeus (17) presented a theoretical treatment which showed that the distribution coefficient should go through a maximum

as the ligand concentration is increased in the external solution. Furthermore, his derivation showed that the distribution coefficient would have its maximum value when the ligand concentration in the outer solution was such that Bjerrum's average ligand number, $\bar{n}$, equaled the ratio of the charge on the central metal ion to the charge on the ligand. Thus the greater the tendency of a central metal ion to form complex ions with a given ligand, the greater would be the value of D_{max}. Also, the maximum would occur at lower concentrations of ligand in the outer solution. Fronaeus' data for cadmium bromide and cadmium iodide support these conclusions very well.

The occurrence of a maximum in the distribution coefficient is not difficult to explain in a qualitative manner if one considers the two types of adsorption processes mentioned earlier. For a system which contains only the ligand form of a metal salt and the ligand salt form of the anion exchange resin, with no other source of ligand present, the resulting equilibrium may be treated either as a non-exchange equilibrium or as an exchange equilibrium. The two points of view are actually equivalent in such a system. For example, if a resin in the chloride form is added to a solution of pure cadmium chloride salt, then it does not matter if one supposes the sorption to occur by

$$Cd^{++}, CdCl_4^{--} + 2\,R^+, 2\,Cl^- = 2\,R^+, CdCl_4^{--} + Cd^{++}, 2\,Cl^-$$

or by

$$Cd^{++}, 2\,Cl^{-} + 2\,R^{+}, 2\,Cl^{-} = 2\,R^{+}, CdCl_4^{--}$$

insofar as the over-all result is concerned. However, the latter must represent much more accurately the "reaction" that actually takes place, since the concentration of the complex ion $CdCl_4^{--}$ is extremely small in dilute aqueous solutions of cadmium chloride. It is therefore reasonable to assume that here the equilibrium distribution of cadmium would be governed primarily by the extent of complexation occurring in the resin phase.

On the other hand, if a sample of resin in the chloride form is added to a cadmium chloride solution which also contains a relatively large amount of some other source of chloride ion, say sodium chloride, then the predominate cadmium species in this solution might well be the complex ion $CdCl_4^{--}$. If this were the case, the most realistic representation of the sorption process would probably be

$$2\,Na^{+}, CdCl_4^{--} + 2\,R^{+}, 2\,Cl^{-} = 2\,R^{+}, CdCl_4^{--} + 2\,Na^{+}, 2\,Cl^{-},$$

wherein actual ion exchange has occurred. Here the relative affinities for the resin of the $CdCl_4^{--}$ complex ion and the simple Cl^{-} ion should be the important factor in determining the distribution coefficient of cadmium, since complexation reactions have been assumed to be essentially complete in both phases.

In the present work the only sources of ligand were the resins and the cadmium halide salts. The various systems

therefore will be treated as non-exchange systems whenever it is convenient to do so.

Stoichiometric mean activity coefficients will be calculated directly from the experimental data. Actual mean ionic activity coefficients, which can be obtained from estimates of the actual "free" ion concentrations, will also be presented. Both types will be compared with the stoichiometric activity coefficients obtained by Nelson and Kraus (28) for salts in which complex ions are presumably not important.

EXPERIMENTAL PROCEDURES

Reagents and Analytical Methods. All cadmium determinations were accomplished by titration for cadmium ion with EDTA (Ethylene-diaminetetraacetic acid). The procedure was essentially the same as that given by Flaschka (3) for zinc.

Two solutions of EDTA were prepared from the disodium salt. Both were standardized against cadmium metal dissolved in the minimum amount of hydrochloric acid. The 0.04209 M EDTA solution was stored in a prepared glass bottle (3); the 0.003850 M EDTA solution was stored in a polyethylene bottle.

Approximately 0.1 M solutions of cadmium nitrate, cadmium chloride, cadmium bromide, and cadmium iodide were prepared from their respective salts. These solutions were standardized with the EDTA solution by the same procedure as used in the analyses.

Most of the halide determinations were by the Volhard method. A few of the chloride determinations were done by the Mohr method.

The anion exchange resin used was Dowex-1, X8, 100-200 mesh. The resin is obtained from the manufacturer in the chloride form. Fine particles present in the commercial product were

removed by stirring a batch of the resin with water in a beaker, allowing the heavier particles to settle out, and then pouring off the "fines". After several such treatments a product was obtained which settled rapidly following agitation.

The bromide form of the resin was prepared by passing an approximate three-fold excess of 0.1 M sodium bromide solution through the resin chloride in a column. The resin was then washed in the column with distilled water until free of excess sodium bromide solution. A 0.1 M potassium iodide solution was used as the conditioning agent to prepare the iodide form of the resin.

All three resin forms were air dried in small shallow dishes for use in the equilibrium studies. In each series of determinations the air-dried resin weights were converted to a dry weight basis by determining the moisture content of the particular batch of air-dried resin used. The moisture content was obtained by drying weighed samples in an oven at 110 degrees centigrade for twenty-four hours.

The capacity of the resin was determined by direct Mohr titration of the resin in the chloride form. The value found was 3.76 milliequivalents per gram of oven-dry resin in the chloride form. This value is 3.22 when expressed as milliequivalents per dry gram of bromide form, 2.79 for the iodide form, and 3.42 for the nitrate form of the resin.

Equilibrium Determinations. The equilibrium distributions

of cadmium salts between the external solution and resin were determined by the batch method. Twenty milliliters of cadmium salt solution were added to each of several Erlenmeyer flasks containing various weighed amounts of air-dried resin in the appropriate form. The mixtures were then agitated by a mechanical shaker for twenty-four hours, a convenient time period which appears to have become almost standard in ion exchange studies of this type.

After equilibrium had been established, aliquot portions of the external solutions were withdrawn by pipette and analyzed. The cadmium and halide molar concentrations in the external solutions were thus determined directly. The amount of cadmium salt in the resin was determined indirectly by difference, since the total amount of cadmium was known. However, in order to do this accurately the volume of the external solution at equilibrium must also be known. The initial volume of solution added was always twenty milliliters, but since partially dried (air-dried) resin was used, the equilibrium solution volume was surely less than twenty milliliters in every case. If the volume of external solution is quite large compared to the total available volume of the resin, and if the amount of sorption of salt is neither very large nor very small, then this effect may be neglected without appreciably altering the results. Since this was not always the case in the determinations here, a small (approximate) correction was applied on the basis of water sorption measurements made on the pure resins.

Resin Volume Determinations. It is customary to express the equilibrium distribution of a diffusible electrolyte as grams (or moles) of salt in the resin phase per dry gram of resin divided by the molality or molarity of the electrolyte in the external solution. It was desired here to express concentrations on the molar scale for both phases. Since the equilibrium measurements gave only an amount of electrolyte in the resin, resin volumes were needed to convert these to molar concentrations.

The centrifuge technique was used for the measurement of water uptake, and this combined with pycnometric data allowed the estimation of resin volumes. The centrifuge technique has been described by a number of authors (20, 21, 28, 29). The apparatus used here was quite simple and is shown in Figure 1. A weighed quantity of air-dried resin of known water content was placed in the filter tube. The filter tube was immersed in water to allow the resin to swell to its equilibrium water content, then removed and placed in the test tube for centrifugation to constant weight. Each time the filter tube was removed for weighing it was quickly capped at both ends with rubber caps to minimize loss of water by evaporation. In this way the water contents of the swollen resins were determined for each resin salt form, expressed as grams of water per dry gram of resin in the appropriate salt form.

After the resin had been centrifuged to constant weight, it was washed into a pycnometer with a stream of water and weighed, water being used as the pycnometric fluid. From this weight, the density of water, and the resin "wet weight", the total volume of the wet swollen resin could be calculated and expressed as milliliters per dry gram of resin in the appropriate salt form.

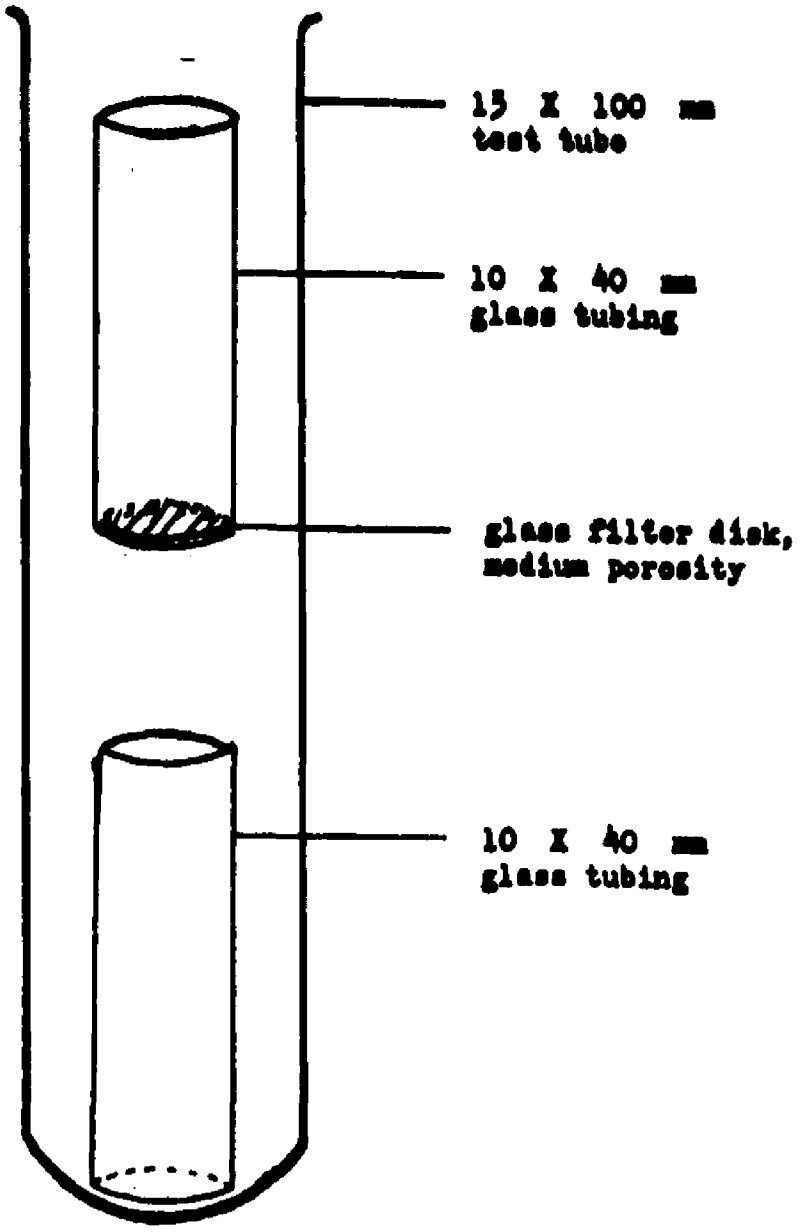

Figure 1. Centrifuge Apparatus for the Resin Wet Weight Determinations.

RESULTS

Resin Volumes. The data for each of the four resin forms are given in Table I. Values given there for the weight of water sorbed, the wet swollen volume, and the available volume refer to one dry gram of resin in the respective salt form.

As was mentioned previously, resin volumes were needed so that resin concentrations could be given on the molar scale. There is a difficulty in doing this aside from those of an experimental nature, for the requisite volumes actually cannot be defined unambiguously. The selection of the volumes to use is therefore arbitrary, but the volumes chosen should have the property of making the molar concentrations derived from them be reasonably comparable to those of ordinary aqueous solutions.

The volumes subsequently used were those called "available volume" in Table I. The method used in arriving at these values will be illustrated for the chloride form of the resin. The weight of water sorbed, 0.801 grams, corresponds to a volume of 0.786 ml., using Gregor's value (20) of 17.7 ml. for the average partial molar volume of water in a strong-base anion exchange resin. The available resin volume is taken to be this volume of 0.786 ml. plus the volume occupied

TABLE I.

RESIN VOLUMES

Resin form	Chloride	Bromide	Iodide	Nitrate
Grams of water sorbed	0.801	0.526	0.338	0.533
Wet-swollen volume (ml.)	1.613	1.253	0.975	1.367
Available volume (ml.)	0.842	0.576	0.407	0.666
Resin matrix volume per meq., (ml.)	0.205	0.210	0.204	-----

by the chloride ions in one gram of the resin chloride. The latter can be estimated from the capacity of the resin, Avogadro's number, and the radius of the chloride ion given by Pauling (11):

$$V_{Cl} = 3.76 \times (6.02 \times 10^{20}) \times 4/3 \ (1.81 \times 10^{-8})^3$$

$$= 0.056 \text{ ml.}$$

The volume of the resin matric (including the quaternary ammonium functional group) per equivalent of resin should be a constant independent of the resin salt form. It can be calculated from the relation

$$V_{matrix} = \frac{\text{(total volume per gram)} - \text{(available volume per gram)}}{\text{(milliequivalents per gram)}}$$

The values obtained for the three halide forms of the resin are also given in Table I. The agreement seemed good enough to justify a reverse calculation for the available volume of the resin nitrate, since there was considerable uncertainty as to what value to use for the effective radius of the nitrate ion.

The available volumes in Table I are values which, with the assumptions involved, apply to pure resins equilibrated with water. To use these values in systems where cadmium salts are also present, it is necessary to make the additional assumption that the presence of the cadmium salts does not appreciably affect these volumes. Nelson and Kraus (28) have suggested that at least in

some cases the resin beads may be treated as "a cage with constant volume". In the present case, no change in the settled volume was detected upon equilibration of resin halide with cadmium halide in small volumes. It thus seems reasonable to assume here that such volume changes as do occur are small, since changes in volume of only a few per cent are observable in the settled volume.

Equilibrium Distributions. Data for the six systems studied are given in Tables II-VII. "Milliequivalents of resin" is the product of the resin dry weight and the previously determined capacity of the particular resin form. "Available resin volume" is the product of the resin dry weight and the appropriate value from Table I.

In the cadmium nitrate-resin halide systems (Tables V-VII) the resin at equilibrium was a mixture of the nitrate and halide forms. The available resin volumes that were used in arriving at the molar concentrations were estimated by linear interpolation on a mole fraction basis. For example, available volumes from Table I are 0.146 and 0.195 ml. per meq. for the iodide and nitrate forms, respectively. Available volumes of the mixed nitrate-iodide resin form were then calculated from

$$V_{(NO_3^-I^-)} = 0.146 + 0.049\ X_{NO_3^-}$$

Bonner, et. al., (16) found such a linear relationship to hold for various cation exchange equilibria.

TABLE II.

EQUILIBRIUM CONCENTRATIONS IN THE CADMIUM CHLORIDE-RESIN CHLORIDE SYSTEM.

Millimoles of $CdCl_2$ taken	Meq. of resin taken	Available volume (ml.), resin phase	C	D	$\bar{C}$	$\bar{D}$
1.728	0.654	0.146	0.0758	0.1516	1.495	7.47
1.728	0.984	0.220	0.0693	0.1386	1.600	7.57
1.728	1.572	0.353	0.0610	0.1220	1.485	7.43
1.728	2.45	0.549	0.0482	0.0964	1.422	7.31
1.728	3.22	0.721	0.0416	0.0832	1.271	7.01

"C" is the stoichiometric molar concentration of cadmium.
"D" is the stoichiometric molar concentration of chloride.
Resin phase quantities are denoted by a bar over the symbols.

TABLE III.

EQUILIBRIUM CONCENTRATIONS IN THE CADMIUM BROMIDE-RESIN BROMIDE SYSTEM.

Millimoles of $CdBr_2$ taken	Meq. of resin taken	Available volume (ml.), resin phase	C	D	$\bar{C}$	$\bar{D}$
1.948	0.286	0.0511	0.0901	0.1802	2.94	11.46
1.948	0.592	0.1061	0.0824	0.1648	2.88	11.32
1.948	0.863	0.1546	0.0752	0.1504	2.92	11.41
1.948	1.420	0.254	0.0614	0.1228	2.88	11.32
1.948	2.13	0.382	0.0458	0.0916	2.74	11.03
1.948	2.84	0.509	0.0307	0.0614	2.64	10.88

TABLE IV.

EQUILIBRIUM CONCENTRATIONS IN THE CADMIUM IODIDE-RESIN IODIDE SYSTEM.

Millimoles of CdI_2 taken	Meq. of resin taken	Available volume (ml.), resin phase	C	D	$\bar{C}$	$\bar{D}$
1.952	0.268	0.0392	0.0935	0.1870	2.12	11.08
1.952	0.509	0.0744	0.0900	0.1800	2.11	11.06
1.952	1.061	0.1550	0.0819	0.1638	2.08	11.00
1.952	1.629	0.238	0.0733	0.1466	2.08	11.00
1.952	2.10	0.308	0.0666	0.1332	2.05	10.93

TABLE V.

EQUILIBRIUM CONCENTRATIONS IN THE CADMIUM NITRATE-RESIN CHLORIDE SYSTEM.

Millimoles of $Cd(NO_3)_2$ taken	Meq. of Resin taken	Available volume (ml.), resin phase	C	D	$\bar{C}$	$\bar{D}$
2.060	0.586	0.114	0.1031	0.0234	0.0961	1.060
2.060	1.761	0.344	0.1023	0.0775	0.142	0.695
2.060	2.22	0.445	0.0977	0.0919	0.191	0.946
2.060	2.34	0.468	0.0988	0.0937	0.278	1.090
2.060	2.95	0.591	0.0974	0.1042	0.286	1.577

TABLE VI.

EQUILIBRIUM CONCENTRATIONS IN THE CADMIUM NITRATE-RESIN BROMIDE SYSTEM.

Millimoles of $Cd(NO_3)_2$ taken	Meq. of resin taken	Available volume (ml.), resin phase	C	D	$\overline{C}$	$\overline{D}$
2.060	0.565	0.1071	0.1019	0.0253	0.289	0.568
2.060	1.132	0.200	0.0973	0.0336	0.650	2.17
2.060	1.589	0.302	0.0925	0.0353	0.772	2.95
2.060	1.690	0.321	0.0915	0.0357	0.789	3.06
2.060	2.23	0.424	0.0852	0.0370	0.915	3.54
2.060	2.78	0.529	0.0784	0.0362	1.00	3.92

TABLE VII.

EQUILIBRIUM CONCENTRATIONS IN THE CADMIUM NITRATE-RESIN IODIDE SYSTEM.

Millimoles of $Cd(NO_3)_2$ taken	Meq. of resin taken	Available volume (ml.), resin phase	C	D	$\overline{C}$	$\overline{D}$
2.060	0.510	0.0913	0.0982	0.00711	1.118	4.13
2.060	1.030	0.1822	0.0923	0.00946	1.257	4.62
2.060	1.518	0.270	0.0859	0.01062	1.395	4.84
2.060	2.02	0.352	0.0808	0.01105	1.324	5.13
2.060	2.56	0.440	0.0748	0.01297	1.340	5.25

TREATMENT OF DATA

Cadmium Halide Complexes. It has been known for many years that cadmium halide solutions exhibit anomolous behavior toward certain physical measurements. In 1923 Lewis and Randall (9) compared the activity coefficients of cadmium chloride solutions with those of barium chloride solutions and noted a significant divergence at concentrations as low as 0.001 moles per liter. They stated "...that cadmium chloride cannot be regarded as a strong electrolyte."

In succeeding years a considerable amount of evidence has accumulated which indicates that cadmium halide solutions contain a variety of complex cadmium halide species in addition to simple (hydrated) cadmium and halide ions. Furthermore, it has become customary to think of the formation of these complexes as occurring through a step-wise process with each step being described by an equilibrium constant (formation constant, stability constant, etc.).

$$Cd^{++} + Hal^{-} = CdHal^{+}$$

$$(CdHal^{+}) = k_1 (Cd^{++}) (Hal^{-})$$

$$CdHal^{+} + Hal^{-} = CdHal_2$$

$$(CdHal_2) = k_2 (CdHal^+)(Hal^-)$$

$$CdHal_{n-1}^{2-(n-1)} + Hal^- = CdHal_n^{2-n}$$

$$(CdHal_n^{2-n}) = k_n (CdHal_{n-1}^{2-(n-1)}) (Hal^-)$$

It is often more convenient to use the gross formation constants which are defined as the equilibrium constants for the formation of the complexes from cadmium ion and halide ion.

$$(CdHal^+) = K_1 (Cd^{++})(Hal^-) \qquad K_1 = k_1$$

$$(CdHal_2) = K_2 (Cd^{++})(Hal^-)^2 \qquad K_2 = k_1 \cdot k_2$$

$$(CdHal_n^{2-n}) = K_n (Cd^{++})(Hal^-)^n$$

$$K_n = k_1 \cdot k_2 \cdot \ldots \cdot k_n$$

Values of the formation constants for the cadmium halide complexes have been determined by a number of workers who often used different methods under a variety of conditions. A recent compilation of formation constants (2) is available for these and numerous other systems. The formation constants reported in the literature are general concentration quotients based on molar concentrations. Hence the parentheses used in the above equations and in the discussion to follow signify a concentration in moles per liter.

It seems to have been generally assumed that the maximum coordination number of cadmium ion for halide ions in aqueous solution is four. Thus, values for four formation constants (or less)

have been reported for these systems. The values reported by different authors for the same system often agree only as to order of magnitude, even when determined by the same method and presumably under essentially the same conditions. One wishing to use the reported constants is faced with an assortment of values and with very little to serve as a guide in making a selection. It was decided here to perform all the calculations in duplicate, using two sets of constants that differ markedly.

Riley and Gallafent (30) reported the following values for the gross formation constants of the cadmium halides:

	K_1	K_2	K_3	K_4
$CdCl_2$	100	400	500	1000
$CdBr_2$	150	1250	2500	1×10^4
CdI_2	260	2500	1×10^5	1.4×10^6

These values were calculated from potentiometric titrations. The total cadmium concentration was 0.01 M throughout, while the total halide concentration varied from 0.01 M to 2.0 M. Since no attempt was made to control the ionic strength, it varied over the range 0.04-2.0 during the course of the measurements.

Leden (26) reported the following values for the cadmium halides:

	K_1	K_2	K_3	K_4
$CdCl_2$	38.5	170	260	(850)
$CdBr_2$	57	220	2100	5×10^3
CdI_2	120	500	1×10^5	3.1×10^6

These values were also calculated from potentiometric titrations. Both the total concentrations of cadmium and halide were varied during the course of the measurements, but the ionic strength was held constant at 3.0 by the addition of the necessary amounts of sodium perchlorate. Leden does not report a value of K_4 for cadmium chloride, although he did presume the existence of the $CdCl_4^{--}$ ion in small amounts in his solutions. The value of K_4 given in parentheses is from Knoblock and cited by Leden (26).

Once the values of the formation constants have been selected, there are in addition to the four relationships described by these constants, the material balance relations

$$(Cd) = (Cd^{++}) + (CdHal^{+}) + (CdHal_2) + (CdHal_3^{-}) + (CdHal_4^{--})$$

$$(Hal) = (Hal^{-}) + (CdHal^{+}) + 2(CdHal_2) + 3(CdHal_3^{-}) + 4(CdHal_4^{--}).$$

By incorporation of the gross formation constants, these two equations may be written in terms of the equilibrium concentrations

of free (hydrated) cadmium and halide ions.

$$(Cd) = (Cd^{++}) + K_1(Cd^{++})(Hal^-) + K_2(Cd^{++})(Hal^-)^2 + K_3(Cd^{++})(Hal^-)^3 + K_4(Cd^{++})(Hal^-)^4$$

$$(Hal) = (Hal^-) + K_1(Cd^{++})(Hal^-) + 2K_2(Cd^{++})(Hal^-)^2 + 3K_3(Cd^{++})(Hal^-)^3 + 4K_4(Cd^{++})(Hal^-)^4$$

The total cadmium concentration, (Cd), and the total halide concentration, (Hal), may be treated as constants which have been experimentally determined. For convenience as well as for aesthetic reasons, let (Cd) be given the symbol C, let (Hal) be D, (Cd^{++}) be x, and (Hal^-) be y. The last two equations may then be written as

$$K_4xy^4 + K_3xy^3 + K_2xy^2 + K_1xy + x - C = 0$$

and

$$4K_4xy^4 + 3K_3xy^3 + 2K_2xy^2 + K_1xy + y - D = 0.$$

They must be solved simultaneously for x and y.

Several methods are available for the solution of simultaneous nonlinear equations (10), all of which involve either successive approximations or the method of iteration. The Newton-Raphson method was chosen. Let (x_o, y_o) be initial guesses as to the desired roots of the functions

$$F(x, y) = 0$$

$$G(x, y) = 0.$$

One seeks to obtain corrections, Δx and Δy, to x_o and y_o such that

$$x = x_o + \Delta x$$

$$y = y_o + \Delta y$$

and

$$F(x_o + \Delta x, y_o + \Delta y) = 0$$

$$G(x_o + \Delta x, y_o + \Delta y) = 0.$$

The last two of the above equations may be expanded by Taylor's theorem to give

$$F(x + \Delta x, y + \Delta y) = F(x_o, y_o) + F_x(x_o, y_o) \cdot \Delta x + F_y(x_o, y_o) \cdot \Delta y + \ldots = 0$$

$$G(x + \Delta x, y + \Delta y) = G(x_o, y_o) + G_x(x_o, y_o) \cdot \Delta x + G_y(x_o, y_o) \cdot \Delta y + \ldots = 0$$

where $F_x(x_o, y_o)$ is the partial derivative of the function F with respect to x evaluated at (x_o, y_o), etc. If terms of order higher than the first are ignored in the expansion, there result two linear equations in two unknowns, Δx and Δy.

$$F_x(x_o, y_o) \cdot \Delta x + F_y(x_o, y_o) \cdot \Delta y = -F(x_o, y_o)$$

$$G_x(x_o, y_o) \cdot \Delta x + G_y(x_o, y_o) \cdot \Delta y = -G(x_o, y_o).$$

These are solved for Δx and Δy to get new values of x and y :

$$x_1 = x_o + \Delta x$$

$$y_1 = y_o + \Delta y.$$

The new functions and their partial derivatives are evaluated at (x_1, y_1), and the process is repeated to the desired degree of accuracy.

Program for the IBM 650 Computer. The actual numerical solution of the equations presented in the preceding section could involve a great deal of labor. Fortunately, the services of an IBM 650 digital computer were available. The program was written in FOR TRANSIT, a method of programming which permits the programmer to give the computer instructions in a form that resembles ordinary algebraic expressions quite closely. These instructions are punched into cards which then undergo triple translation through three runs on the computer. The output of the last phase of the translation is an optimized machine-language version of the original FOR TRANSIT program (1, 4).

The program in FOR TRANSIT is reproduced in Figure 2. It can be as easily read as ordinary algebraic equations if one observes the few simple conventions. The usual symbols are used for addition, subtraction and division. An asterisk denotes multiplication; a double asterisk denotes exponentiation (e.g., B**3 means B^3). Capital letters are used exclusively, and subscripts cannot be used (e.g., E_1 must be written simply as E1). In an expression containing several operations, parentheses are used to show the desired sequence of the operations whenever there is a

possiblity of ambiguity. Also, some restrictions are placed on the letters which can be used to represent variables and constants (4). In the FOR TRANSIT statement, "C" is the total concentration of cadmium and "D" is the total concentration of halide as before. However, the concentration of free cadmium ion is now called "A" rather than "x", and the concentration of free halide ion is "B" rather than "y". The gross formation constants K_1, K_2, K_3, and K_4 are written as E1, E2, E3, and E4.

Either an actual word or an abbreviation of the word (or words) is used to represent instructions and functions. Thus the function

$$(Cd^{++}) + K_1(Cd^{++})(Hal^-) + K_2(Cd^{++})(Hal^-)^2 + K_3(Cd^{++})(Hal^-)^3 + K_4(Cd^{++})(Hal^-)^4 = C$$

is called "F1", and

$$(Hal^-) + K_1(Cd^{++})(Hal^-) + 2K_2(Cd^{++})(Hal^-)^2 + 3K_3(Cd^{++})(Hal^-)^3 + 4K_4(Cd^{++})(Hal^-)^4 = D$$

is called "F2". The derivative of the first function with respect to the variable (Cd^{++}) is designated by "DF1A", the derivative of the second function with respect to the variable (Hal^-) is designated by "DF2B", etc. The symbols ΔA and ΔB are written simply as "DELA" and "DELB", respectively.

The data needed to solve the two above equations are the

Statement Number	Continue	FORTRAN STATEMENT
101		READ 1, E1, E2, E3, E4
1		READ 1, A, B, C, D
102		IF (A) 2, 101, 2
2		F1 = A ≠ E1 * A * B ≠ E2 *
	1	A * B ** 2 ≠ E3 * A * B ** 3
	2	≠ E4 * A * B ** 4 - C
3		F2 = B ≠ E1 * A * B ≠ 2 * E2 *
	1	A * B ** 2 ≠ 3 * E3 * A * B ** 3
	2	4 * E4 * A * B ** 4 - D
4		DF1A = 1 ≠ E1 * B ≠ E2 *
	1	B ** 2 ≠ E3 * B ** 3 ≠
	2	E4 * B ** 4
5		DF1B = E1 * A ≠ 2 * E2 * A * B
	1	≠ 3 * E3 * A * B ** 2 ≠
	2	4 * E4 * A * B ** 3
6		DF2A = E1 * B ≠ 2 * E2 *
	1	B ** 2 ≠ 3 * E3 * B ** 3 ≠
	2	4 * E4 * B ** 4
7		DF2B = 1 ≠ E1 * A ≠ 4 *
	1	E2 * A * B ≠ 9 * E3 * A *
	2	B ** 2 ≠ 16 * E4 * A * B ** 3
8		DELA = (DF1B * F2 - DF2B *
	1	F1) / (DF1A * DF2B - DF2A *
	2	DF1B)
9		DELB = (DF1A * F2 - DF2A *
	1	F1) / (DF2A * DF1B - DF1A *
	2	DF2B)
10		A = A ≠ DELA
11		B = B ≠ DELB
12		IF (ABSF(DELA / A) -
	1	1.E-4) 14, 14, 2

Figure 2. The For Transit Program.

Statement Number	Continue	FORTRAN STATEMENT
13		IF (ABSVF (DELB / B) -
	1	1.E-4) 14, 14, 2
14		A1 = E1 * A * B
		A2 = E2 * A * B ** 2
		A3 = E3 * A * B ** 3
		A4 = E4 * A * B ** 4
15		PUNCH 1, A, B, C, A1, A2,
	1	A3, A4
16		GO TO 1
17		END

Figure 2. The For Transit Program (continued).

total cadmium concentration, C, the total halide concentration, D, an initial guess of the free cadmium ion concentration, A, an initial guess of the free halide concentration, B, and the four complex formation constants E1, E2, E3, and E4. These data were punched into cards in the so-called "floating point" form. Figure 3 shows an example of a data sheet from which data cards were punched. The initial guess of the cadmium ion concentration went into "word 1", the initial guess of the halide ion concentration went into "word 2", the experimentally determined total cadmium concentration went into "word 3", and the experimentally determined total halide concentration went into "word 4". On the constants card, E1, E2, E3, and E4 went into words 1, 2, 3, and 4, respectively. Each "word", consisting of a possible 10 digits, therefore represents one number. In floating point notation, each number is understood to have a decimal point preceding the first digit, and the last two digits of the 10 digit word is the exponent plus 50. For example, the number 0.005 would be written as 5000000048, the number 252.0 would be written as 2520000053, etc.

With the data cards prepared, the computer is told to

1) read in values of the formation constants from the punch cards
2) read in the initial guesses of (Cd^{++}) and (Hal^{-}), along with

FORTRANSIT DATA FORM

Word 1		Word 2		Word 3		Word
Mantissa	Exp	Mantissa	Exp	Mantissa	Exp	Mantissa
312	49	104	50	758	49	152
283	49	945	49	693	49	139
250	49	835	49	610	49	122
197	49	660	49	482	49	964
172	49	570	49	416	49	832
410	48	137	49	100	49	200
820	48	274	49	200	49	400
123	49	411	49	300	49	600
369	49	123	50	900	49	180
410	49	137	50	100	50	200
000	00	000	00	000	00	000
100	53	440	55	500	53	100
200	47	16	51	1495	51	747
500	47	14	51	160	51	757
270	47	16	51	1485	51	743
160	47	18	51	1422	51	731
930	46	20	51	1271	51	701
000	00	00	00	0000	00	000

Figure 3. Sample of a For Transit Data Form.

the values of the total cadmium and total halide concentrations for the system.

3) evaluate the two functions, F1 and F2, and their partial derivatives

4) use the six numbers obtained from step 3 to find ΔA and ΔB, then use these to determine new values of A and B (e.g., A_1 and B_1)

5) if either $\Delta A/A_1$ or $\Delta B/B_1$ is greater than 10^{-4}, go back and repeat the calculations using $A = A_1$ and $B = B_1$

6) if neither $\Delta A/A_1$ nor $\Delta B/B_1$ is greater than 10^{-4}, then punch out the desired answers: (Cd^{++}), (Hal^-), $(CdHal^+)$, $(CdHal_2)$, $(CdHal_3^-)$ and $(CdHal_4^{--})$, i.e., punch A, B, A1, A2, A3, and A4. (The total concentration of cadmium, C, was punched in the answer card for identification purposes.)

The time required by the computer to calculate an answer varied with the proximity of the initial guesses to the desired roots. On an average, the time that elapsed between punch operations was about twenty-five seconds.

The results of the calculations with the constants of Riley and Gallafent are given in Tables VIII-XIII. The results obtained by use of Leden's formation constants are in Tables XIV-XIX.

The Calculation of Activity Coefficient Ratios and Resin Phase Activity Coefficients. Stoichiometric activity coefficient ratios for the cadmium halides were calculated from the relation

$$\frac{\bar{f}_{\pm}}{f_{\pm}} = \left(\frac{(Cd)\,(Hal)^2}{(\overline{Cd})\,(\overline{Hal})^2} \right)^{1/3}$$

where a bar is used to designate the resin phase. The necessary data are the stoichiometric molar concentrations of cadmium and halide for both phases, and these are given in Tables II-VII for the six systems studied. The resulting values of $\bar{f}/f$ (written hereafter as $\bar{f}/f$) are recorded in Tables XX-XXV.

Ratios of the actual mean ionic activity coefficients, $\bar{g}/g$, were calculated from the above equation by using the "actual" molar concentrations of cadmium ion and halide ion in place of the stoichiometric values. The necessary data are the ion concentrations computed from the complex formation functions, and these data are tabulated in Tables VIII-XIX. The value of $\bar{g}/g$ depends in part upon the formation constants that are used in evaluating the ion concentrations, and since two sets of formaconstants were used, two values of $\bar{g}/g$ can be calculated for each equilibrium. An asterisk has been used to identify the activity coefficients based on Leden's formation constants; the others are based on the formation constants of Riley and Gallafent. Values of $\bar{g}/g$ and $\bar{g}^*/g^*$ are given in Tables XX-XXV.

TABLE VIII.

CALCULATED IONIC CONCENTRATIONS FOR THE CADMIUM CHLORIDE-RESIN CHLORIDE SYSTEM.

Solution Phase

$(Cd^{++})\cdot 10^3$	$(Cl^-)\cdot 10^2$	$(CdCl^+)\cdot 10^2$	$(CdCl_2)\cdot 10^3$	$(CdCl_3^-)\cdot 10^4$	$(CdCl_4^{--})\cdot 10^5$
7.83	6.71	5.25	14.10	11.82	15.86
7.68	6.29	4.84	12.17	9.58	12.10
7.52	5.71	4.29	9.80	6.99	7.98
7.12	4.79	3.41	6.53	3.91	3.75
6.87	4.28	2.94	5.04	2.69	2.31

TABLE VIII.

Continued

Resin Phase

$(Cd^{++}) \cdot 10^5$	(Cl^-)	$(CdCl^+) \cdot 10^2$	$(CdCl_2) \cdot 10^2$	$(CdCl_3^-) \cdot 10^1$	$(CdCl_4^{--})$
6.62	2.02	1.337	10.80	2.73	1.101
10.45	1.814	1.895	13.75	3.12	1.131
6.61	2.02	1.333	10.75	2.71	1.093
5.44	2.10	1.144	9.62	2.53	1.062
3.44	2.31	0.795	7.34	2.12	0.978

TABLE IX.

CALCULATED IONIC CONCENTRATIONS FOR THE CADMIUM BROMIDE-RESIN BROMIDE SYSTEM.

Solution Phase

$(Cd^{++})\cdot 10^3$	$(Br^-)\cdot 10^2$	$(CdBr^+)\cdot 10^2$	$(CdBr_2)\cdot 10^2$	$(CdBr_3^-)\cdot 10^3$	$(CdBr_4^{--})\cdot 10^4$
5.89	6.03	5.33	2.68	3.24	7.81
5.78	5.72	4.96	2.37	2.71	6.20
5.67	5.41	4.60	2.08	2.25	4.87
5.43	4.76	3.88	1.541	1.468	2.80
5.10	3.92	3.00	0.980	0.768	1.205
4.65	2.96	2.06	0.508	0.300	0.355

TABLE IX.

Continued

Resin Phase

$(Cd^{++})\cdot 10^4$	(Br^-)	$(CdBr^+)\cdot 10^2$	$(CdBr_2)\cdot 10^1$	$(CdBr_3^-)\cdot 10^1$	$(CdBr_4^{--})\cdot$
2.62	0.942	3.71	2.91	5.48	2.06
2.30	0.971	3.35	2.71	5.27	2.05
2.52	0.950	3.60	2.85	5.41	2.06
2.30	0.971	3.35	2.71	5.27	2.05
1.570	1.065	2.51	2.22	4.74	2.02
1.067	1.171	1.875	1.830	4.29	2.01

TABLE X.

CALCULATED IONIC CONCENTRATIONS FOR THE CADMIUM IODIDE-RESIN IODIDE SYSTEM.

Solution phase

$(Cd^{++}) \cdot 10^3$	$(I^-) \cdot 10^2$	$(CdI^+) \cdot 10^2$	$(CdI_2) \cdot 10^2$	$(CdI_3^-) \cdot 10^2$	$(CdI_4^{--}) \cdot 10^3$
6.25	3.01	4.89	1.414	1.702	7.16
6.10	2.98	4.73	1.358	1.620	6.76
5.76	2.92	4.37	1.226	1.432	5.85
5.39	2.84	3.98	1.687	1.234	4.91
5.10	2.77	3.67	0.977	1.082	4.20

TABLE X.

Continued

Resin Phase

$(Cd^{++}) \cdot 10^8$	(I^-)	$(CdI^+) \cdot 10^5$	$(CdI_2) \cdot 10^4$	$(CdI_3^-) \cdot 10^2$	(CdI_4^{--})
2.96	2.66	2.04	5.22	5.55	2.06
2.86	2.67	1.99	5.12	5.48	2.05
2.59	2.73	1.84	4.84	5.29	2.03
2.59	2.73	1.84	4.84	5.29	2.03
2.38	2.78	1.72	4.61	5.13	1.998

TABLE XI.

CALCULATED IONIC CONCENTRATIONS FOR THE CADMIUM NITRATE-RESIN CHLORIDE SYSTEM.

Solution Phase

$(Cd^{++}) \cdot 10^2$	$(Cl^-) \cdot 10^2$	$(CdCl^+) \cdot 10^2$	$(CdCl_2) \cdot 10^3$	$(CdCl_3^-) \cdot 10^4$	$(CdCl_4^{--}) \cdot 10^6$
8.24	0.249	2.05	0.204	0.00635	0.00316
4.18	1.372	5.73	3.14	0.539	1.48
3.09	1.995	6.17	4.92	1.228	4.90
3.08	2.03	6.27	5.90	1.299	5.28
2.56	2.54	6.50	6.59	2.09	10.60

TABLE XI.

Continued

Resin Phase

$(Cd^{++})\cdot 10^3$	$(Cl^-)\cdot 10^1$	$(CdCl^+)\cdot 10^2$	$(CdCl_2)\cdot 10^2$	$(CdCl_3^-)\cdot 10^2$	$(CdCl_4^{--})\cdot 10^2$
0.105	7.75	0.815	2.53	2.45	3.80
0.969	3.82	3.70	5.65	2.70	2.06
0.769	4.79	3.68	7.06	4.23	4.05
1.391	4.37	6.09	10.65	5.82	5.10
0.355	7.43	2.64	7.84	7.28	10.81

TABLE XII.

CALCULATED IONIC CONCENTRATIONS FOR THE CADMIUM NITRATE-RESIN BROMIDE SYSTEM.

Solution Phase

$(Cd^{++})\cdot 10^2$	$(Br^-)\cdot 10^3$	$(CdBr^+)\cdot 10^2$	$(CdBr_2)\cdot 10^3$	$(CdBr_3^-)\cdot 10^6$	$(CdBr_4^{--})\cdot 10^7$
7.89	1.915	2.26	0.361	1.385	0.1061
6.73	2.90	2.93	0.707	4.10	0.475
6.13	3.29	3.03	0.833	5.49	0.723
6.10	3.39	3.06	0.864	5.86	0.795
5.31	3.90	3.11	1.009	7.86	1.226
4.75	4.20	2.99	1.045	8.78	1.474

TABLE XII.

Continued

Resin Phase

$(Cd^{++}) \cdot 10^3$	$(Br^-) \cdot 10^1$	$(CdBr^+) \cdot 10^2$	$(CdBr_2) \cdot 10^1$	$(CdBr_3^-) \cdot 10^1$	$(CdBr_4^{--}) \cdot 10^1$
8.88	1.010	13.46	1.133	0.229	0.0925
1.309	3.59	7.04	2.10	1.510	2.17
0.523	5.17	4.06	1.751	1.811	3.75
0.463	5.41	3.75	1.696	1.836	3.98
0.445	5.74	3.83	1.833	2.10	4.83
0.382	6.18	3.54	1.823	2.25	5.57

TABLE XIII.

CALCULATED IONIC CONCENTRATIONS FOR THE CADMIUM NITRATE-RESIN IODIDE SYSTEM.

Solution Phase

$(Cd^{++}) \cdot 10^2$	$(I^-) \cdot 10^4$	$(CdI^+) \cdot 10^2$	$(CdI_2) \cdot 10^5$	$(CdI_3^-) \cdot 10^6$	$(CdI_4^{--}) \cdot 10^8$
9.14	2.86	0.679	1.864	0.213	0.0851
8.33	4.14	0.897	3.57	0.592	0.344
7.58	5.08	1.001	4.89	0.993	0.706
7.04	5.66	1.036	5.65	1.280	1.015
6.27	7.40	1.205	8.57	2.54	2.63

TABLE XIII.

Continued

Resin Phase

$(Cd^{++}) \cdot 10^3$	$(I^-) \cdot 10^1$	$(CdI^+) \cdot 10^2$	$(CdI_2) \cdot 10^2$	$(CdI_3^-) \cdot 10^1$	$(CdI_4^{--}) \cdot 10^1$
0.716	1.639	3.05	4.81	3.15	7.23
0.816	1.632	3.46	5.43	3.55	8.12
2.34	1.242	7.55	9.02	4.48	7.79
0.225	2.36	1.383	3.14	2.97	9.82
0.162	2.59	1.090	2.71	2.81	10.20

TABLE XIV.

CALCULATED IONIC CONCENTRATIONS FOR THE CADMIUM CHLORIDE-RESIN CHLORIDE SYSTEM.

Solution Phase

$(Cd^{++})\cdot 10^2$	$(Cl^-)\cdot 10^2$	$(CdCl^+)\cdot 10^2$	$(CdCl_2)\cdot 10^3$	$(CdCl_3^-)\cdot 10^4$	$(CdCl_4^{--})\cdot 10^5$
1.560	7.32	4.40	14.23	15.94	38.16
1.514	6.91	4.03	12.29	12.98	29.32
1.456	6.32	3.54	9.88	9.54	19.71
1.338	5.37	2.76	6.55	5.38	9.43
1.264	4.83	2.35	5.01	3.71	5.85

TABLE XIV.

Continued

Resin Phase

$(Cd^{++})\cdot 10^5$	(Cl^-)	$(CdCl^+)\cdot 10^3$	$(CdCl_2)\cdot 10^2$	$(CdCl_3^-)\cdot 10^1$	$(CdCl_4^{--})\cdot$
12.02	1.857	8.59	7.05	2.00	1.216
20.76	1.634	13.06	9.42	2.35	1.257
11.98	1.855	8.56	7.01	1.990	1.207
9.51	1.950	7.14	6.15	1.835	1.170
5.57	2.180	4.68	4.50	1.502	1.071

TABLE XV.

CALCULATED IONIC CONCENTRATIONS FOR THE CADMIUM BROMIDE-RESIN BROMIDE SYSTEM.

Solution Phase

$(Cd^{++}) \cdot 10^2$	$(Br^-) \cdot 10^2$	$(CdBr^+) \cdot 10^2$	$(CdBr_2) \cdot 10^2$	$(CdBr_3^-) \cdot 10^3$	$(CdBr_4^{--}) \cdot 10^3$
1.357	6.78	5.25	1.374	8.89	1.436
1.311	6.49	4.85	1.214	7.51	1.160
1.267	6.18	4.46	1.066	6.29	0.926
1.175	5.53	3.70	0.790	4.17	0.548
1.055	4.63	2.78	0.497	2.19	0.242
0.905	3.54	1.825	0.249	0.841	0.0708

TABLE XV.

Continued

Resin Phase

$(Cd^{++})\cdot 10^4$	(Br^-)	$(CdBr^+)\cdot 10^2$	$(CdBr_2)\cdot 10^1$	$(CdBr_3^-)\cdot 10^1$	$(CdBr_4^{--})$
5.91	0.897	3.02	1.045	8.95	1.910
5.04	0.931	2.68	0.963	8.56	1.900
5.64	0.906	2.91	1.020	8.83	1.905
5.04	0.931	2.68	0.963	8.56	1.900
3.21	1.041	1.902	0.765	7.60	1.884
2.05	1.164	1.362	0.612	6.80	1.885

TABLE XVI.

CALCULATED IONIC CONCENTRATIONS FOR THE CADMIUM IODIDE-RESIN IODIDE SYSTEM.

Solution Phase

$(Cd^{++})\cdot 10^2$	$(I^-)\cdot 10^2$	$(CdI^+)\cdot 10^2$	$(CdI_2)\cdot 10^3$	$(CdI_3^-)\cdot 10^2$	$(CdI_4^{--})\cdot 10^2$
1.467	2.36	4.15	4.07	1.921	1.404
1.424	2.34	4.01	3.92	1.838	1.337
1.324	2.32	3.68	3.55	1.647	1.183
1.217	2.28	3.33	3.16	1.444	1.021
1.134	2.25	3.06	2.86	1.286	0.896

TABLE XVI.

Continued

Resin Phase

$(Cd^{++}) \cdot 10^8$	(I^-)	$(CdI^+) \cdot 10^6$	$(CdI_2) \cdot 10^5$	$(CdI_3^-) \cdot 10^2$	(CdI_4^{--})
1.421	2.63	4.48	4.90	2.57	2.09
1.373	2.64	4.36	4.80	2.54	2.08
1.239	2.70	4.02	4.53	2.45	2.05
1.239	2.70	4.02	4.53	2.45	2.05
1.136	2.75	3.76	4.31	2.37	2.03

TABLE XVII.

CALCULATED IONIC CONCENTRATIONS FOR THE CADMIUM NITRATE-RESIN CHLORIDE SYSTEM.

Solution Phase

$(Cd^{++})\cdot 10^2$	$(Cl^-)\cdot 10^2$	$(CdCl^+)\cdot 10^2$	$(CdCl_2)\cdot 10^3$	$(CdCl_3^-)\cdot 10^4$	$(CdCl_4^{--})\cdot 10^5$
8.54	0.527	1.732	0.403	0.0324	0.00559
5.22	2.26	4.54	4.52	1.560	1.151
4.25	2.97	4.85	6.36	2.88	2.80
4.25	3.01	4.94	6.57	3.03	2.99
3.76	3.54	5.13	8.01	4.34	5.02

TABLE XVII.

Continued

Resin Phase

$(Cd^{++})\cdot 10^3$	$(Cl^-)\cdot 10^1$	$(CdCl^+)\cdot 10^2$	$(CdCl_2)\cdot 10^2$	$(CdCl_3^-)\cdot 10^2$	$(CdCl_4^{--})\cdot 10^2$
0.1904	7.50	0.550	1.822	2.09	5.13
2.29	3.57	3.15	4.96	2.71	3.16
1.086	4.41	3.07	5.98	4.04	5.83
3.52	3.94	5.34	9.29	5.60	7.22
0.769	6.81	2.02	6.07	6.33	14.10

TABLE XVIII.

CALCULATED IONIC CONCENTRATIONS FOR THE CADMIUM NITRATE-RESIN BROMIDE SYSTEM.

Solution Phase

$(Cd^{++}) \cdot 10^2$	$(Br^-) \cdot 10^3$	$(CdBr^+) \cdot 10^2$	$(CdBr_2) \cdot 10^4$	$(CdBr_3^-) \cdot 10^5$	$(CdBr_4^{--}) \cdot 10^6$
8.13	4.36	2.02	3.40	1.416	0.1470
7.08	6.39	2.58	6.37	3.89	0.592
6.52	7.14	2.65	7.32	4.99	0.849
6.40	7.32	2.67	7.55	5.27	0.920
5.74	8.21	2.68	8.52	6.68	1.306
5.19	8.66	2.56	8.56	7.08	1.460

TABLE XVIII.

Continued

Resin Phase

$(Cd^{++})\cdot 10^3$	$(Br^-)\cdot 10^1$	$(CdBr^+)\cdot 10^2$	$(CdBr_2)\cdot 10^2$	$(CdBr_3^-)\cdot 10^1$	$(CdBr_4^{--})\cdot 10^1$
24.57	1.014	14.20	5.56	0.538	0.1299
4.82	3.00	8.24	9.53	2.73	1.947
1.605	4.54	4.15	7.28	3.15	3.41
1.376	4.79	3.76	6.95	3.18	3.62
1.302	5.10	3.78	7.44	3.62	4.39
1.069	5.55	3.38	7.25	3.84	5.08

TABLE XIX.

CALCULATED IONIC CONCENTRATIONS FOR THE CADMIUM NITRATE-RESIN IODIDE SYSTEM.

Solution Phase

$(Cd^{++})\cdot 10^2$	$(I^-)\cdot 10^3$	$(CdI^+)\cdot 10^3$	$(CdI_2)\cdot 10^5$	$(CdI_3^-)\cdot 10^5$	$(CdI_4^{--})\cdot 10^7$
9.17	0.589	6.48	1.591	0.1875	0.342
8.37	0.849	8.53	3.02	0.513	1.351
7.64	1.034	9.48	4.08	0.845	2.71
7.10	1.148	9.77	4.67	1.073	3.82
6.34	1.482	11.28	6.97	2.07	9.49

TABLE XIX.

Continued

Resin Phase

$(Cd^{++}) \cdot 10^3$	$(I^-) \cdot 10^1$	$(CdI^+) \cdot 10^2$	$(CdI_2) \cdot 10^2$	$(CdI_3^-) \cdot 10^1$	(CdI_4^{--})
3.49	0.923	3.86	1.487	2.75	0.786
4.42	0.901	4.79	1.790	3.15	0.899
12.20	0.689	10.09	2.90	3.99	0.853
0.867	1.408	1.465	0.860	2.42	1.058
0.546	1.597	1.046	0.696	2.22	1.100

In addition to the activity coefficient ratios, the resin phase activity coefficients $\bar{f}$, $\bar{g}$ and $\bar{g}^*$ are included in Table XX, Table XXI, and Table XXII. These were calculated from the activity coefficient ratios and the appropriate values of the activity coefficients f, g and g* for the aqueous phase. The stoichiometric activity coefficients, f, were taken from the literature: those of Harned and Fitzgerald (23) for cadmium chloride, those of Bates (14) for cadmium bromide, and those of Bates and Vosburgh (15) for cadmium iodide.

Values for g and g* were estimated from Kielland's (24) individual ion activity coefficients, γ . Ionic strengths for the external solutions were calculated from the concentrations and charges of the individual ionic species given in Tables VIII-X and Tables XIV-XVI. The values of γ for cadmium ion and for halide ion were read from graphs of γ vs. ionic strength. The mean activity coefficients g and g* were then obtained from the relation

$$g = \left(\gamma_{Cd} \gamma_{Hal}^2 \right)^{1/3}$$

Only the activity coefficient ratios are given for the cadmium nitrate-resin halide systems (Tables XXIII-XXV). Activity coefficients for the cadmium halides in cadmium nitrate

solutions would be needed to obtain $\bar{f}$, and these were not available. Furthermore, the ionic strength in the external solution was too high in these systems to permit the use of Kielland's table. Hence, only the activity coefficient ratios are given for these systems.

TABLE XX.

ACTIVITY COEFFICIENT RATIOS AND RESIN PHASE ACTIVITY COEFFICIENTS FOR CADMIUM CHLORIDE IN THE CADMIUM CHLORIDE-RESIN CHLORIDE SYSTEM.

C	$\bar{f}/f$	$\bar{g}/g$	$\bar{g}^*/g^*$	$\bar{f}$	$\bar{g}$	$\bar{g}^*$
0.0758	0.0261	0.508	0.586	0.00681	0.32	0.36
0.0693	0.0244	0.445	0.506	0.00659	0.28	0.31
0.0610	0.0233	0.450	0.520	0.00636	0.29	0.32
0.0482	0.0193	0.408	0.474	0.00604	0.27	0.30
0.0416	0.0166	0.409	0.481	0.00553	0.27	0.31

TABLE XXI.

ACTIVITY COEFFICIENT RATIOS AND RESIN PHASE ACTIVITY COEFFICIENTS FOR CADMIUM BROMIDE IN THE CADMIUM BROMIDE-RESIN BROMIDE SYSTEM.

C	$\bar{f}/f$	$\bar{g}/g$	$\bar{g}^*/g^*$	$\bar{f}$	$\bar{g}$	$\bar{g}^*$
0.0901	0.0196	0.452	0.508	0.00392	0.29	0.31
0.0824	0.0183	0.443	0.502	0.00381	0.28	0.31
0.0752	0.0165	0.418	0.471	0.00356	0.27	0.29
0.0614	0.0136	0.384	0.435	0.00319	0.25	0.28
0.0458	0.0105	0.353	0.402	0.00282	0.24	0.26
0.0307	0.00718	0.303	0.345	0.00228	0.21	0.23

TABLE XXII.

ACTIVITY COEFFICIENT RATIOS AND RESIN PHASE ACTIVITY COEFFICIENTS FOR CADMIUM IODIDE IN THE CADMIUM IODIDE-RESIN IODIDE SYSTEM.

C	$\bar{f}/f$	$\bar{g}/g$	$\bar{g}^*/g^*$	$\bar{f}$	$\bar{g}$	$\bar{g}^*$
0.0935	0.0233	3.00	4.36	0.00261	1.885	2.62
0.0900	0.0224	2.98	4.34	0.00258	1.887	2.63
0.0819	0.0206	2.94	4.29	0.00249	1.883	2.63
0.0733	0.0184	2.82	4.12	0.00236	1.830	2.57
0.0666	0.0169	2.77	4.06	0.00230	1.820	2.56

TABLE XXIII.

ACTIVITY COEFFICIENT RATIOS FOR CADMIUM CHLORIDE IN THE CADMIUM NITRATE-RESIN CHLORIDE SYSTEM.

C	$\bar{f}/f$	$\bar{g}/g$	$\bar{g}^*/g^*$
0.1031	0.0805	0.201	0.281
0.1023	0.0964	0.382	0.451
0.0977	0.169	0.412	0.475
0.0988	0.297	0.363	0.441
0.0974	0.114	0.439	0.509

TABLE XXIV.

ACTIVITY COEFFICIENT RATIOS FOR CADMIUM BROMIDE IN THE CADMIUM NITRATE-RESIN BROMIDE SYSTEM.

C	$\bar{f}/f$	$\bar{g}/g$	$\bar{g}^*/g^*$
0.1019	0.0887	0.147	0.183
0.0973	0.0330	0.150	0.187
0.0925	0.0258	0.168	0.215
0.0915	0.0251	0.172	0.220
0.0852	0.0217	0.177	0.225
0.0784	0.0188	0.179	0.227

TABLE XXV.

ACTIVITY COEFFICIENT RATIOS FOR CADMIUM IODIDE IN THE CADMIUM NITRATE-RESIN IODIDE SYSTEM.

C	$\bar{f}/f$	$\bar{g}/g$	$\bar{g}^*/g^*$
0.0982	0.00639	0.0730	0.102
0.0923	0.00675	0.0868	0.119
0.0859	0.00667	0.0820	0.112
0.0808	0.00657	0.122	0.176
0.0748	0.00697	0.147	0.215

DISCUSSION

T. S. Lee (8) has made the following summarizing statement concerning activity coefficients: "The mean activity coefficient of an electrolyte is a catchall empirical factor that provides for many independent and interdependent sources of deviation from ideality." The magnitude of an activity coefficient may therefore provide some indication as to the importance of these "sources of deviation" in a given system, but it can give no clue as to their nature.

The activity coefficient ratios which have been determined to date for non-exchange electrolytes have invariably followed the same general pattern. The ratio $\bar{f}/f$ increases only slowly with the external solution molality (or molarity) at concentrations above about 2 molal and is not far from unity. At low concentrations of diffusible electrolyte in the external solution (<0.1 molal), $\bar{f}/f$ is considerably less than unity and decreases rapidly with concentration in the external solution.

Nelson and Kraus (28) have reported stoichiometric activity coefficients for cobalt chloride and barium chloride in a strong-base anion exchanger. A few of their values are given

TABLE XXVI.

ACTIVITY COEFFICIENT RATIOS AND RESIN PHASE ACTIVITY COEFFICIENTS FOR COBALT CHLORIDE AND BARIUM CHLORIDE.*

Cobalt Chloride

m	$\bar{f}/f$	$\bar{f}$
0.002	0.0087	0.007
0.02	0.092	0.06
0.05	0.192	0.11
0.20	0.41	0.20

Barium Chloride

0.02	0.09	0.06
0.20	0.43	0.19

* The data in this table are from Nelson and Kraus (28).

in Table XXVI for comparison with the cadmium halides. Their activity coefficients are based on the molal rather than the molar scale, but the concentrations of interest here are small enough to make the two essentially the same.

The stoichiometric activity ratios and the resin phase activity coefficients for the cadmium halides are given in Tables XX-XXII. These values are plotted vs. external solution concentration in Figure 4 and Figure 5.

Values of $\bar{f}/f$ for cobalt chloride are some ten times larger than f/f for the cadmium halides at comparable external solution concentrations. The values of $\bar{f}$ for cobalt chloride are twenty to forty times larger. These observations are not unexpected in view of the complexation known to occur with the cadmium halides. The extent of complex formation is of course much greater in the resin phase because of the high ligand concentration in that phase.

It is possible, at least in principle, to separate from the stoichiometric activity coefficient the contribution made by complex ion formation. This procedures gives $\bar{g}/g$ and $\bar{g}^*/g^*$, which may be considered to have the following significance. Only that portion of cadmium halide which is completely ionized is considered in both phases. Complex cadmium halide species are involved only in so much as their presence affects the activity coefficients of the "free" cadmium and halide ions. Of course, the concentration of free halide ion in the resin phase must be taken as the

sum of that furnished by the resin and by the imbibed cadmium halide.

Regardless of whatever complex cadmium halide species are present in each of the two phases, at equilibrium the product of the cadmium ion activity and the square of the halide ion activity must be the same in the two phases (provided the same standard state is chosen for the two phases). To calculate activity coefficient ratios from this relation presupposes that the requisite ionic concentrations are accurately known.

The complex ion formation constants exactly applicable to each of the two phases would surely not be the same, since in practice these are concentration quotients and not thermodynamic constants. This is intuitively a logical conclusion, although it is perhaps not possible even to estimate what the differences might be. It is possible that use of the same formation for both phases (as was done here) overestimates the ionic concentrations in one phase and underestimates them in the other, thereby enhancing the error in the calculated activity coefficient ratios.

If the calculated ionic concentrations of free cadmium and halide ions are reasonably reliable values, then the activity coefficient ratios and resin phase coefficients derived from them should not be too different from those for cobalt chloride and barium chloride in solutions of similar ionic strength. However,

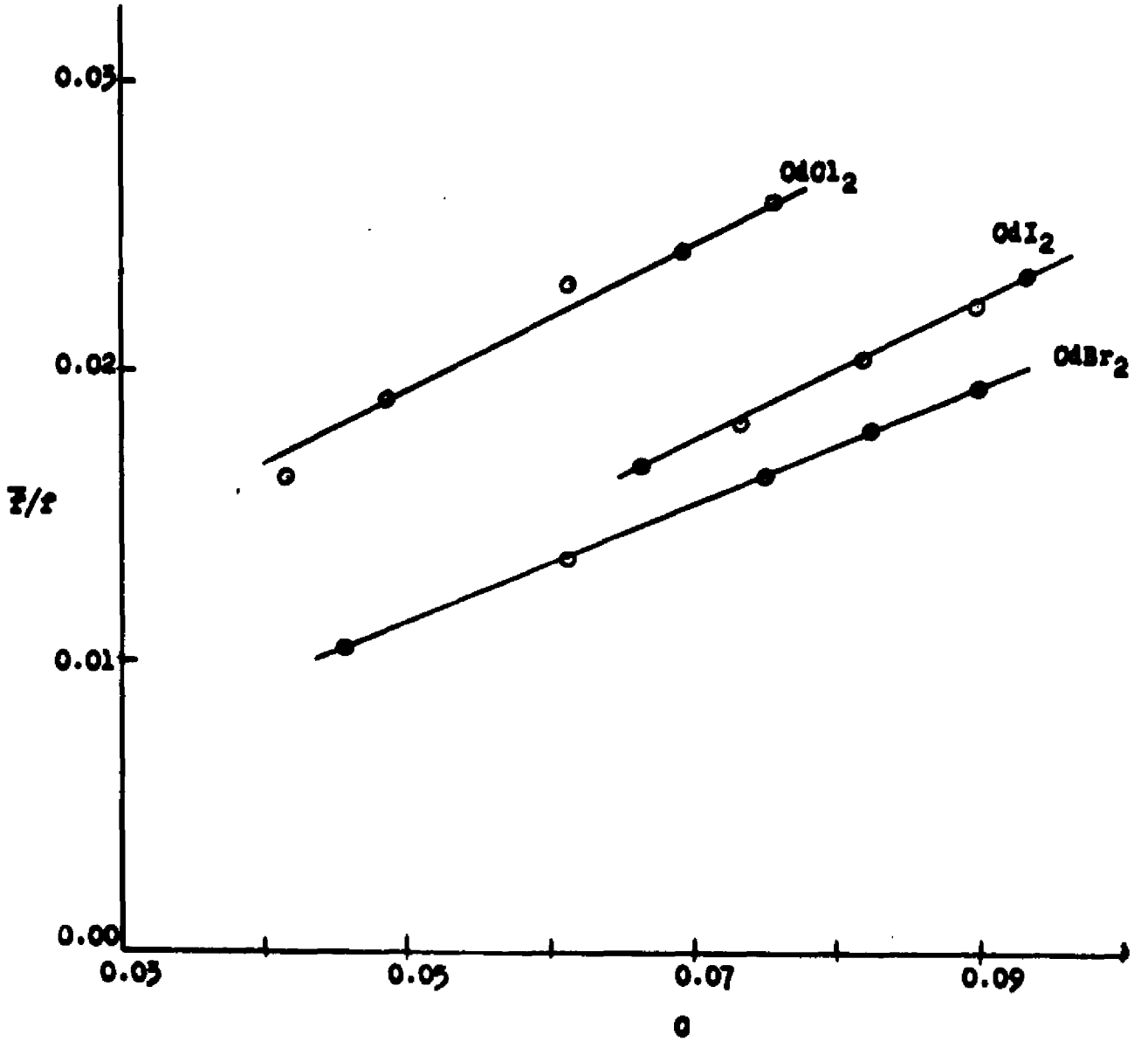

Figure 4. Stoichiometric Activity Coefficient Ratios of the Cadmium Halides vs. Cadmium Halide Molarity in the External Solution.

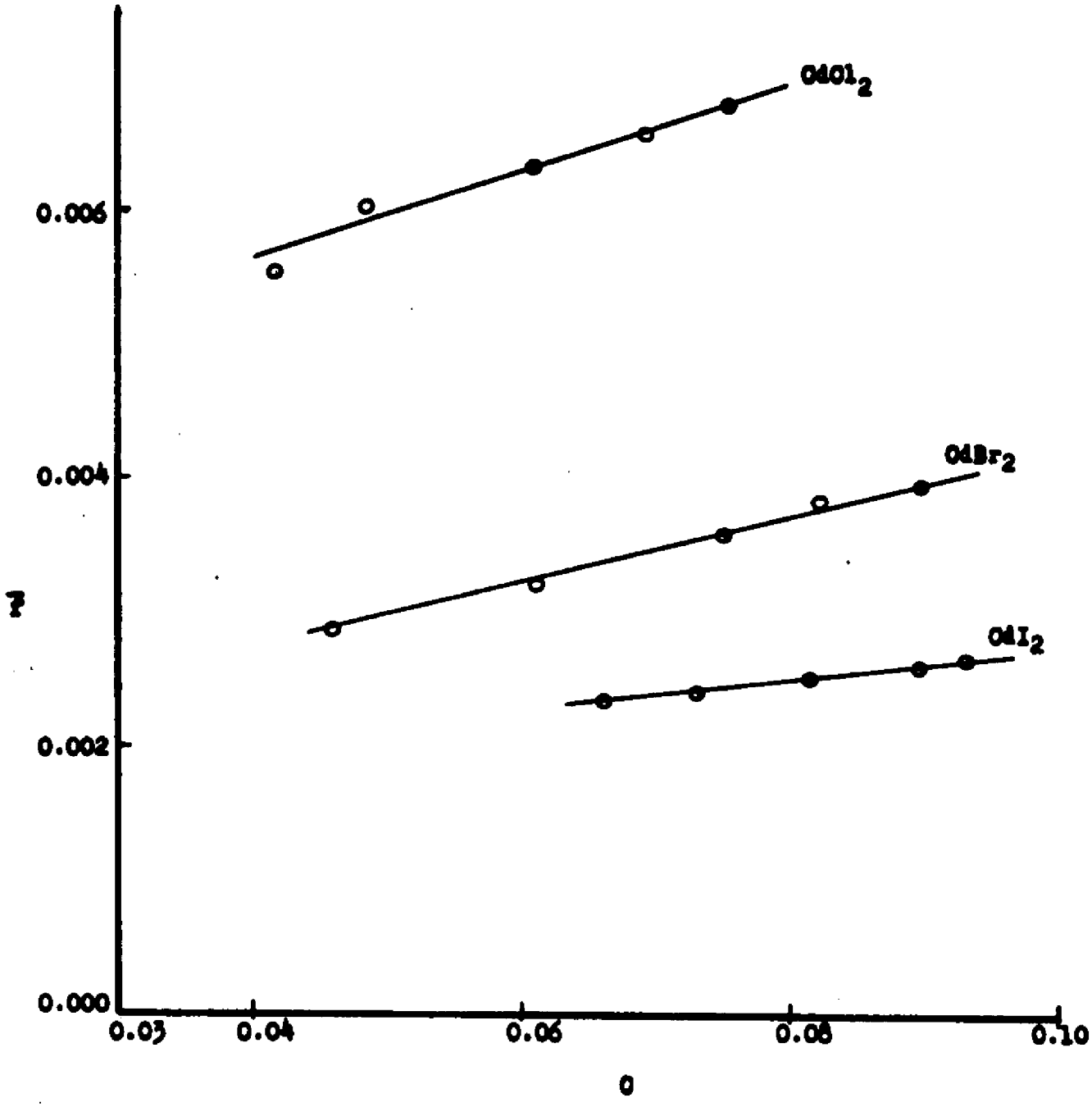

Figure 5. Stoichiometric Activity Coefficients of the Cadmium Halides in the Resin Phase vs. Cadmium Halide Molarity in the External Solution.

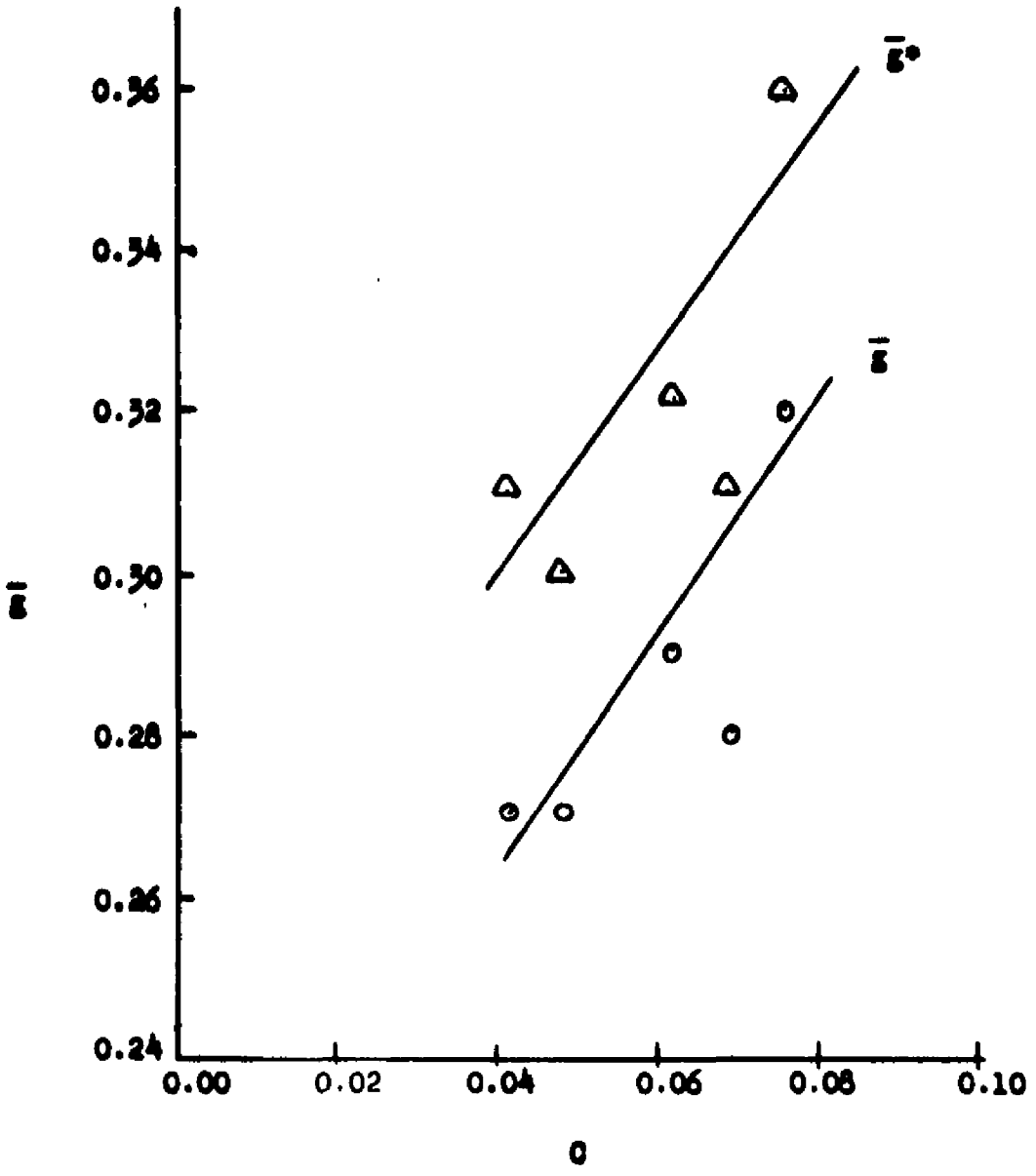

Figure 6. The Calculated Actual Mean Ionic Activity Coefficients of Cadmium Chloride in the Resin Phase vs. Cadmium Chloride Molarity in the External Solution.

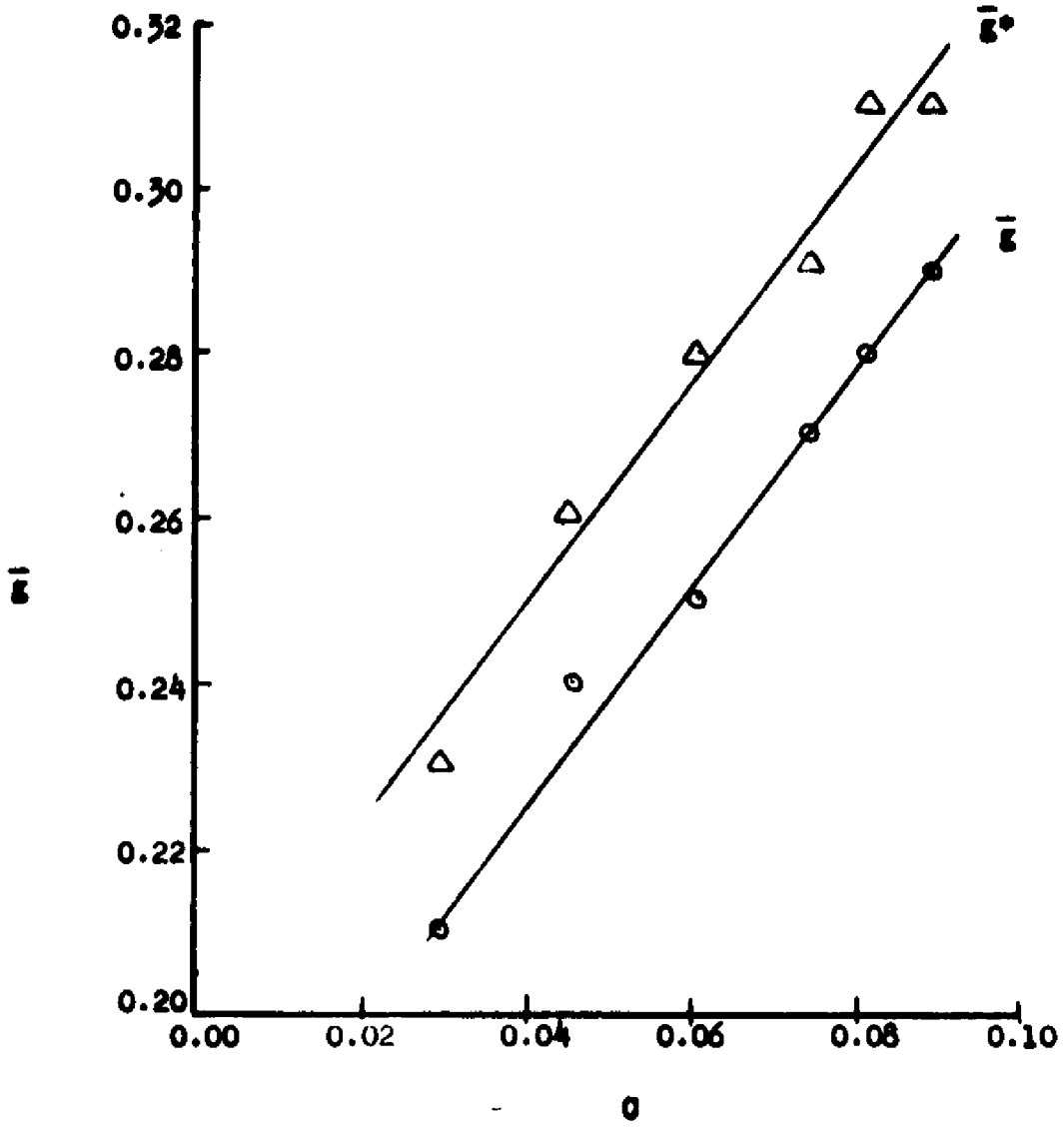

Figure 7. The Calculated Actual Mean Ionic Activity Coefficients of Cadmium Bromide in the Resin Phase vs. Cadmium Bromide Molarity in the External Solution.

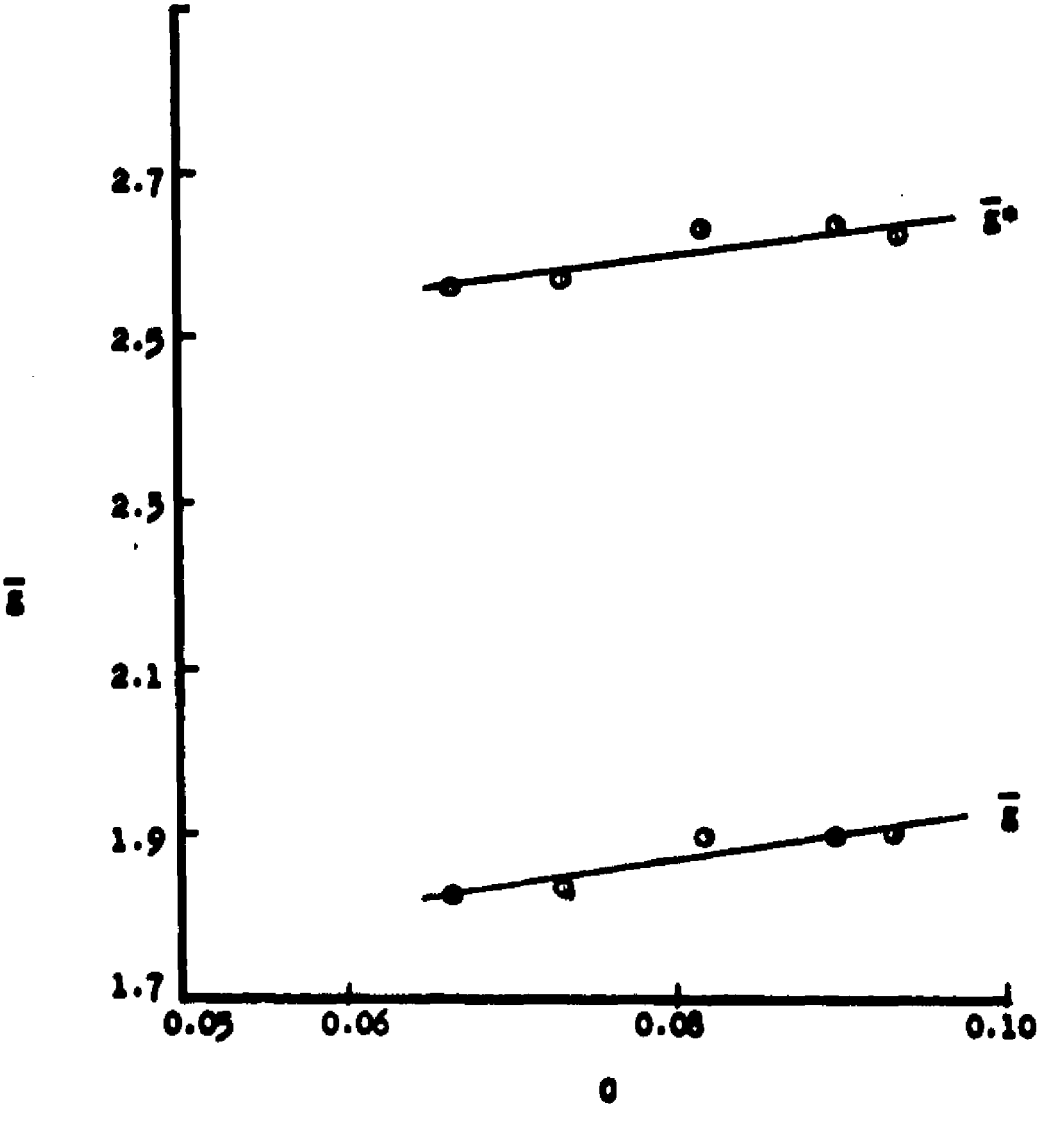

Figure 8. The Calculated Actual Mean Ionic Activity Coefficients of Cadmium Iodide in the Resin Phase vs. Cadmium Iodide Molarity in the External Solution.

the fact must be taken into consideration that the nature of the resin may have been substantially altered in the case of the cadmium halides. Here the counter ions at equilibrium will be to a large extent the complex species $CdHal_3^-$ and $CdHal_4^{--}$, whereas in the case of cobalt and barium halides, the counter ions at equilibrium are presumably the simple anions just as in the pure resin. If there is greater interaction between the quaternary ammonium groups of the resin and the complex anions than there is between these groups and simple anions, the activity coefficients of non-exchange electrolytes present in the resin would not be expected to be as low in the former case as in the latter.

Some data of Nelson and Kraus (28) have shown that $\bar{f}/f$ for hydrochloric acid at a given molality increases and approaches unity as the concentration of the resin functional groups decreases (i.e., with resins of decreasing cross-linkage). Such an effect would be expected if the strong electric field existing within the resin were reduced by any means, such as, for example, by the presence of the more polarizible $CdHal_3^-$ and $CdHal_4^{--}$ complex ions.

The values of g/g and g^*/g^* for cadmium chloride (Table XX) are larger than the corresponding activity coefficient ratios for cobalt chloride by a factor of about four. The same is true

for cadmium bromide (Table XXI): $\bar{g}/g$ and $\bar{g}^*/g^*$ are roughly four times larger than $\bar{f}/f$ for cobalt chloride. The values of $\bar{g}/g$ are reasonable in both cases, and the agreement between them is gratifying in view of the fact that the complex formation constants are quite different for cadmium chloride and cadmium bromide.

Similar results for cadmium iodide would have provided additional support for the validity of the results for the other two. The activity coefficient ratios, $\bar{g}/g$ and $\bar{g}^*/g^*$, calculated for this system are quite large (Table XXII). However, it is possible that in aqueous solutions of cadmium iodide, the cadmium ion exhibits a coordination number greater than four. The concentrations of free cadmium ion and free iodide ion calculated on the basis of a maximum coordination of four would then be grossly in error for solutions of high iodide ion concentration (e.g., in the resin phase).

Halclar (22) has found by thermometric titrations what appears to be conclusive evidence for the CdI_5^{-3} ion in cadmium solutions of high iodide ion concentration. Unfortunately, a formation constant for this species has apparently never been reported. If such a species exists, it could be important and might well predominate in the resin phase because of the high concentration of iodide ion that exists in that phase. The results

that were obtained here for the concentrations of free cadmium ion and iodide ion in the external solutions were probably not much in error, since the iodide ion concentrations were too low in the external solutions for the five-coordinated species to be important.

Some qualitative observations based on the experimental data of Tables XX-IV suggest rather convincingly the presence of the CdI_5^{---} ion in the resin phase. Assume that in each of the three systems all of the cadmium ion in the resin is coordinated to four halide ions, then calculate the free halide ion concentration from the relation

(free halide) = (total halide) - (4) (total cadmium).

The free halide concentrations calculated in this way are about 1.5 M for the chloride, near zero for the bromide, and about 2.5 M for the iodide. The result for the iodide is completely anomalous, for it would be expected to be even less than that for the bromide if four were the true maximum coordination number of cadmium ion for iodide ion. A coordination number of five for the cadmium iodide would give a more reasonable value for the free iodide concentration.

The cadmium nitrate-resin halide systems are

considerably more complicated than those containing only cadmium halide. In addition to the various equilibria involving the cadmium halide complexes, there is the usual type of ion exchange equilibrium between nitrate ion and halide ion, and also possibly complexation of cadmium ion with nitrate ion. The latter is perhaps not very important, since the formation constants are small. However, nitrate complexes in the resin phase may not have been entirely negligible in those cases where the concentrations of nitrate ion in the resin were large. Even if cadmium nitrate complexation were not involved, the presence of the nitrate ion would surely affect the values of the activity coefficient ratios for cadmium halide.

None of the numerous equilibria involved are independent and even a qualitative elucidation would be difficult. Consequently, not much can be said concerning the activity coefficient ratios calculated for these systems and given in Tables XXIII-XXV. In general, values of $\bar{g}/g$ are lower than those for the pure cadmium halide-resin halide systems. The ratios increase with decreasing cadmium concentration in the external solutions for the most part, in contrast to the usual behavior. This increase is perhaps a result of the fact that the systems are becoming more nearly "like" the cadmium halide-resin halide systems, since

the total amount of halide present (i.e., the amount of resin taken) was increasing in this direction, while the amount of cadmium nitrate taken was the same throughout. This effect may have predominated over the tendency toward smaller values of the activity coefficient ratios with decreasing electrolyte concentration in the external solutions.

CONCLUSION

The equilibrium between a strong-base anion exchange resin and a solution of pure cadmium halide is more correctly described as a non-exchange type of equilibrium. When the entire system is at equilibrium, cadmium ions and halide ions are in equilibrium with the various complex cadmium halide species in each of the two phases, while freely diffusible species such as Cd^{++} ion and Hal^{-} ion must also be in equilibrium across the phase boundary separating the two phases.

Actual mean ionic activity coefficient ratios and resin phase activity coefficients that can be derived from the calculated actual free ion concentrations present in cadmium chloride and cadmium bromide solutions are not very different from the stoichiometric activity coefficients for simple electrolytes in non-exchange systems. The differences that are observed can possibly be within the limits of error of the calculations so that an attempt to interpret these differences actually cannot be justified. However, the properties of the resin phase must surely be altered to a greater extent by the adsorption of the

complex cadmium halides than by the imbition of simple electrolytes such as barium chloride, and probably in such a way as to increase the activity coefficient toward unity: the more polarizable anionic metal complexes interact more strongly with the resin functional groups than do simple anions. Such interactions have been suggested on numerous occasions in the past to account for the high affinities for the resin shown by some complex anionic metal species, but the importance of these interactions has perhaps been overemphasized.

The idea that anionic metal complexes show abnormally high affinities for anion exchange resins doubtlessly has been perpetuated in large measure by the custom of reporting data for these systems in the form of gross distribution coefficients for the central metal. If the complexation reactions that occur in both phases were taken quantitatively into account so that the equilibrium distribution could be considered from the point of view of an equilibrium involving the transport of free (hydrated) metal ion across the phase boundary, then the distribution of metal ion in complex systems would very likely resemble closely the distributions found in simple ion exchange systems. A similarity between the two types of systems has been demonstrated here by comparing the actual mean ionic activity coefficients for the cadmium halides in a strong-base resin with the stoichiometric mean ionic activity coefficients for barium chloride and cobalt chloride. The same procedure could be applied to numerous other systems for which reliable values of the complex ion formation constants are available.

SELECTED BIBLIOGRAPHY

Books

1. Andree, R. V.,

   Programming the IBM 650 Magnetic Drum Computer and Data-Processing Machine.

   Holt, Rinehart and Winston, Inc., New York (1958).

2. Bjerrum, J., et. al.,

   Stability Constants. Part II: Inorganic Ligands

   Special Publication No. 7 of the Chemical Society, London (1958).

3. Flaschka, H. A.,

   EDTA Titrations.

   Pergamon Press Inc., New York (1959), p. 75.

4. IBM Reference Manual, For Transit Automatic Coding System for the IBM 650 Data Processing System.

   Form C28-4028, International Business Machines Corporation, Data Processing Division, White Plains, New York (1959).

5. Kitchener, J. A.,

"Physical Chemistry of Ion-exchange Resins", Modern Aspects of Electrochemistry, No. 2. Edited by J. O'M. Bockris.

Academic Press Inc., New York (1959), pp. 87-159.

6. Kraus, K. A.,

"Ion Exchange", Trace Analysis. Edited by J. H. Yoe and H. J. Koch.

John Wiley and Sons, Inc., New York (1957), pp. 84-86.

7. Kraus. K. A. and Nelson, F.,

"Anion Exchange Studies of Metal Complexes", The Structure of Electrolytic Solutions. Edited by W. J. Hamer.

John Wiley and Sons, Inc., New York (1959), pp. 340-364.

8. Lee, T. S.,

"Chemical Equilibrium and the Thermodynamics of Reactions," Treatise on Analytical Chemistry, Part I, Theory and Practice, Vol. 1. Edited by I. M. Kilthoff, et. al.

The Interscience Encyclopedia, Inc., New York (1959) p. 238.

9. Lewis, G. N. and Randall, M.,

Thermodynamics and the Free Energy of Chemical Substances.

McGraw-Hill Book Company, Inc., New York (1923), pp. 360-362.

10. Nielsen, K. L.,

Methods in Numerical Analysis.

The MacMillan Company, New York (1956), pp. 201-202.

11. Pauling. L.,

The Nature of the Chemical Bond. Second Edition.

Cornell University Press, New York (1948), pp. 343-350.

Periodicals

12. Analytical Chemistry, 32, Annual Reviews Edition, pp. 67R-70R (1960), and previous issues of the Annual Reviews editions.

13. Annual Review of Physical Chemistry, 10, pp. 123-144 (1959), and previous issues.

14. Bates, R. G.,

"The Thermodynamics of Bi-univalent Electrolytes, IV. Cadmium Bromide in Aqueous Solution."

J. Am. Chem. Soc., 61, 308 (1939).

15. Bates, R. G. and Vosburgh, W. C.,

"The Activity Coefficients of Cadmium Iodide."

J. Am. Chem. Soc., 59, 1583 (1937).

16. Bonner, O. D., Argersinger, W. J. and Davidson, A. W.,

"Factors Involved in Cation Exchange Equilibria."

J. Am. Chem. Soc., 74, 1044 (1952).

17. Fronaeus, S.,

"On the use of Anion Exchangers for the Study of Complex

Systems."

Svensk Kem. Tidskr., 65, 1 (1953).

18. Gottlieb, M. H., and Gregor, H. P.,

"Studies on Ion Exchange Resins. XI. Activity Coefficients of Diffusible Ions in a Strong Base Anion-Exchange Resin."

J. Am. Chem. Soc., 76, 4639 (1954).

19. Gregor, H. P.,

"Gibbs-Donnan Equilibria in Ion Exchange Resin Systems."

J. Am. Chem. Soc., 73, 642 (1951).

20. Gregor, H. P., Belle, J., and Marcus, R. A.,

"Studies on Ion Exchange Resins. IX. Capacity and Specific Volumes of Quaternary Base Anion Exchange Resins."

J. Am. Chem. Soc., 76, 1984 (1954).

21. Gregor, H. P., Held, K. M. and Bellin, J.,

"Determination of the External Volume of Ion Exchange Resin Paricles."

Anal. Chem., 23, 620 (1951).

22. Halclar, B. C.,

"Studies on Cadmium Iodide Complexes."

J. Indian Chem. Soc., 23, 205 (1946).

23. Harned, H. S. and Fitzgerald, M. E.,

"The Thermodynamics of Cadmium Chloride in Aqueous

Solution from Electromotive Force Measurements."

J. Am. Chem. Soc., 61, 308 (1939).

24. Kielland, J.,

"Individual Activity Coefficients of Ions in Aqueous Solutions."

J. Am. Chem. Soc., 59, 1675 (1937).

25. Kraus, K. A. and Moore, G. E.,

"Anion Exchange Studies. V. Adsorption of Hydrochloric Acid by a Strong Base Anion Exchanger."

J. Am. Chem. Soc., 75, 1457 (1953).

26. Leden, I.,

"Einige potentiometrische Messunger zur Bestimmung der Komplexionen in Cadmiumsalzlosungen."

Z. physik. Chem. (Leipzig), A188, 160 (1941).

27. Masatashi, F.,

"Ion Exchange Resins as Reaction Media for Microdetection Tests."

Chemist-Analyst, 49, No. 1, 4 (1960).

28. Nelson, F. and Kraus, K. A.,

"Anion Exchange Studies, XXIII. Activity Coefficients of Some Electrolytes in the Resin Phase."

J. Am. Chem Soc., 80, 4154 (1958).

29. Pepper, K. W., Reichenberg, D. and Hale, D. K., "Properties of Ion-exchange Resins in Relation to their Structure. Part IV. Swelling and Shrinkage of Sulphonated Polystyrenes of Different Cross-Linking." J. Chem. Soc. (London), 3129 (1952).

30. Riley, H. L. and Gallafent, V., "A Potentiometric Investigation of Electrolytic Dissociation. Part I. Cadmium Halides." J. Chem. Soc. (London), 514 (1932).

VITA

Edward Lyndol Harris was born at Roby, Texas, on November 12, 1933. He received his elementary education in the public schools at Roby, Texas. He attended high school in Sweetwater, Texas, graduating from Newman High School in May of 1952.

In September, 1952, he entered McMurry College, Abilene, Texas. He was awarded the Bachelor of Arts degree by that institution in May, 1956. While attending McMurry College he was married to the former Golda Staton of Sweetwater in June of 1954. They now have a daughter, Toni Lynn, born January 9, 1957, and a son, James Mansel, born January 13, 1960.

In September, 1956, he entered the Graduate School of Louisiana State University, and in August of 1958 he received the Master of Science degree in chemistry. In September of 1958 he again enrolled in the Graduate School of Louisiana State University and is now a candidate for the degree of Doctor of Philosophy.

EXAMINATION AND THESIS REPORT

Candidate: Edward Lyndol Harris

Major Field: Chemistry

Title of Thesis: Cadmium Halide Complexes and Anion Exchange Equilibria

Approved:

Maurice M Vick
Major Professor and Chairman

Richard J. Russell
Dean of the Graduate School

EXAMINING COMMITTEE:

James D. Swalen

Eugene W. Berg

J. T. Edsall

Vincent E. Parker

Date of Examination: April 21, 1961